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THE

PHYSICAL REVIEW.

THE ELECTROMOTIVE FORCE PRODUCED BY THE ACCELERATION OF METALS.

By Richard C. Tolman and T. Dale Stewart.

THE modern theories of electricity have led to the belief that the passage of an electric current through a metal really consists in the progressive motion of "free" electrons contained in the body of the metal itself. If this be true we may now expect a number of effects arising from the *mass* of these electrons which were not predictable on the basis of older theories which thought of electricity as a sort of intangible massless fluid. As examples of such effects, we should expect the rear end of an *accelerated* rod of metal to become negatively charged owing to the lagging behind of the relatively mobile electrons which the metal contains, and should expect the periphery of a *rotating* disk to become negatively charged owing to the action of centrifugal force on the electrons in the disk. Such effects, however, would presumably be very small, owing to the exceedingly small mass probably associated with the electron.

Previous Work with Electrolytic Conductors.

In the case of electrolytes effects such as these have long been known, their experimental determination being far less difficult than with metals owing to the relatively large masses associated with the carriers of electricity in such conductors.

An effect of this kind in electrolytes was first obtained by the *acceleration method* in 1882 by Colley[1] using a tube containing a solution of cadmium iodide and provided with electrodes at the two ends. The tube was given a sudden negative acceleration by dropping it and then bringing it to rest in a box of sand, the small pulse of electricity being noted which flowed through a galvanometer connected in circuit with the electrodes. More elaborate measurements of the effect of acceleration

[1] Colley, Wied. Ann., *17*, p. 55, 1882.

have since been made by Tolman and Osgerby[1] using different electrolytes, potassium, sodium and lithium iodides, and varying both the acceleration and distance between the electrodes. Within the necessarily large limits of error these results were found to agree with those theoretically predicted.

In the case of electrolytes much larger effects can be obtained by the *centrifugal method* than by the acceleration method, and these were first detected by Des Coudres[2] in 1892. Since then one of the present authors,[3] using a very powerful centrifugal machine, has made a systematic study of the effect in four different electrolytes, potassium, sodium and lithium iodides and hydriodic acid, and has found an entirely satisfactory agreement between theory and experiment.

PREVIOUS WORK WITH METALLIC CONDUCTORS.

In the case of metallic conductors, Maxwell,[4] himself, was the first, not only to discuss the nature of the phenomena which would arise if mass of the ordinary kind should be associated with electricity in metals, but also to try experiments to detect the possible effects. He had, however, no means of predicting the presumable size of such effects if they did exist since this was before the development of the electron theory and he merely states the negative results of his experiments without any information as to the dimensions or efficiency of his apparatus. Lodge[5] also reports a negative result for such experiments.

The first attempts to detect such effects of which we have any quantitative information were made by Nichols[6] in 1906. He employed the centrifugal method, using a rotating aluminum disk and making a rubbing contact at the periphery and center with wires, which led to the electrical measuring apparatus. Such rubbing contacts, in particular the one at the rapidly moving periphery, necessarily introduce large and variable electromotive forces; nevertheless from a series of experiments Nichols was able to conclude that the mass of the carrier in metals is less than that of the hydrogen atom.

This centrifugal method of attack, which is by far the most powerful and satisfactory in the case of electrolytes, suffers necessarily in the case of metals from this necessity for some form of rubbing contact at the

[1] Tolman, Osgerby and Stewart, J. Am. Chem. Soc., *36*, p. 466, 1914.

[2] Des Coudres, Wied. Ann., *49*, p. 284, 1893. Ibid., *57*, p. 232, 1896.

[3] Tolman, Proc. Am. Acad., *46*, p. 109, 1910; J. Am. Chem. Soc., *33*, p. 121, 1911.

[4] Maxwell, Treatise on Electricity and Magnetism, 3d edition (1892). Vol. II., pp. 211 et seq.

[5] Lodge, Modern Views of Electricity, 3d edition (1907), p. 39.

[6] Nichols, Physik. Z., *7*, p. 640, 1906.

periphery. In the case of electrolytes the difference in potential between the central and peripheral electrodes can be measured with the help of wires which are led to the center of the rotating apparatus and there make contact with connections leading to the stationary measuring apparatus. In the case of a rotating metal disk, however, if we should make connection with the periphery through a wire led to the center, the electromotive force in this wire, which is inappreciable compared with the electromotive force in electrolytes, would of course be just large enough to neutralize the electromotive force in the disk itself. For this reason the centrifugal method of attack almost necessarily involves some disastrous form of rubbing contact, and the acceleration method, which would give much smaller effects but would also involve much smaller errors, seems more suitable for metals.

Making use for this reason of the acceleration method the authors reported in 1913[1] that the effect in metals, if any, was so small that the mass of the carrier in metals was less than one two-hundredth part of that of the hydrogen atom. With the help of a much more sensitive galvanometer and eliminating one by one a number of accidental effects which appear when greater sensitiveness is reached, the authors have now apparently obtained a real effect due to the mass of the carrier in metals. The results are reported here not only because of the interest naturally attaching to the observation of an effect which has been so long looked for, but also because of the bearing which measurements of this kind have on the theory of the conduction and constitution of metals.

ELEMENTARY THEORY OF THE ACCELERATION EFFECT.

From an elementary point of view we can develop a fairly satisfactory theory of the potentials and currents which would be produced by accelerating a metallic conductor. In the future, making use of a more

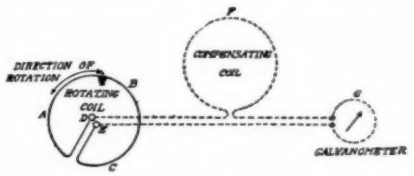


Fig. 1.

intimate knowledge of the structure of matter, it may be possible to develop a more complete theory.

Let us consider the arrangement of conductors actually used in our experiments as shown diagrammatically in Fig. 1.

[1] Tolman, Osgerby and Stewart, loc. cit.

ABC is a coil of wire which can be rotated in either direction about its axis at a high speed and suddenly brought to rest. The two ends of this coil of wire are brought to the center at *D* and *E* and connections made with the external circuit as indicated by the dotted lines. This external circuit contains a compensating coil *F* whose function need not detain us now, and the ballistic galvanometer *G* which measures the pulse of electric current produced on stopping the rotating coil. This pulse of electricity arises from the momentum of the electrons in the rotating coil which causes them to continue in motion after the rotation of the coil has ceased.

Let the length of the moving wire be l, its cross section s, and its resistance R_i. Let the resistance of the external part of the circuit be R_e.

Consider now one equivalent of electrons situated in the rotating coil. If m is the mass associated with an equivalent of electrons (*i. e.*, with $F = 96{,}500$ coulombs of electricity) and v is the tangential velocity of the coil just before stopping, the momentum of these electrons at the instant of stopping will be mv, and the electrons will continue in motion until the mechanical and electrical forces acting on them have destroyed this momentum mv.

Let us now try to analyze the forces acting on one equivalent of electrons in a conductor which is being accelerated.

The Electrical Force.—If E is the difference in electrical potential between the two ends of the wire the potential gradient at any point will be E/l and the *electrical force* acting on one equivalent of electrons (*i. e.*, on $F = 96{,}500$ coulombs of electricity) will be EF/l.

The Frictional Force.—If the electrons are lagging behind the rest of the metal there will be a frictional force acting on them. From the fact that Ohm's law holds in metals we may assume proportionality between such frictional forces and the relative velocity of the metal and the electrons. If U is the mobility of the electron (*i. e.*, the velocity which it attains under unit potential gradient) then U/F will be the velocity which one equivalent of electrons would attain under unit force. Hence if the electrons are lagging behind the rest of the metal with the velocity u the *frictional force* acting per equivalent will be uF/U.

The Acceleration Force.—Besides the frictional force which acts on the electrons because they are lagging behind the conductor, it is evident that there may be an additional mechanical force which would act on the electrons in a conductor which is being accelerated even if they did not lag behind the rest of the metal. From a molecular point of view this force might arise from the fact that the electrons are surrounded by atoms of the metal which are themselves being accelerated and hence

in collision or interaction with these atoms the electrons receive on the average an extra component of momentum in the direction of acceleration. The magnitude of this *accelerational force*, as it might be called, is difficult to estimate. In the case of an accelerated liquid which has the density D and is being given the acceleration a it is evident that each cubic centimeter is being acted on with the force Da, and hence that a body of volume v immersed in such a liquid would be acted on by an accelerational or buoyant force of the amount vDa, this buoyant force being transmitted to the body in question by the surrounding liquid. For this reason in making calculations on accelerated liquids similar to those we are now considering in accelerated metals, the accelerational force acting on one equivalent of dissolved substance was placed equal to $\bar{v}Da$ where $\bar{v}$ was the partial equivalent volume of the solute in question. Even in the case of liquids, however, the justification for such a procedure is not entirely clear, since the buoyant force acting on a substance which after being dissolved and dispersed in a solution has the partial volume $\bar{v}$ would perhaps not necessarily be the same as the force acting on an undispersed body having the same volume v. For this reason in the even more complicated case of solids we may content ourselves with placing the buoyant or accelerational force acting on one equivalent of electrons equal to ka, where k is a constant whose value is for the present unknown. It will be seen that this is in reality equivalent to representing by ka, regardless of the exact nature of their mechanism, any other forces besides those which we have called "electrical" and "frictional," and it may be noted that this has involved the tacit assumption that they are proportional to the acceleration, which in the light of the foregoing discussion is not entirely unreasonable.

From the considerations presented in the three preceding paragraphs we may now place the total force acting on one equivalent of electrons in the interior of an accelerated metal equal to the sum of the electrical, frictional and accelerational forces, giving us

$$f = \frac{EF}{l} + \frac{uF}{U} + ka. \tag{1}$$

If now our conductor is suddenly brought to rest from the velocity v, it is evident that the integral of this force with the time must be equal to the total momentum of the electrons which has to be destroyed, giving us

$$mv = \int_0^\infty \left(\frac{EF}{l} + \frac{uF}{U} + ka \right) dt, \tag{2}$$

where m is the mass of one equivalent of electrons.

E is the potential difference at the two ends of the moving coil and hence is the electromotive force which pushes the current through the external circuit, permitting the substitution

$$E = IR_e + L_e \frac{dI}{dt}, \tag{3}$$

where R_e and L_e are the resistance and inductance of the external circuit.

Furthermore since u is the velocity with which the electrons are lagging behind the metal we may evidently write for the current

$$I = uFCs, \tag{4}$$

where C is the concentration of the electrons in equivalents per cubic centimeter and s is the cross section of the conductor. We may also note, since U is the mobility of the electrons (*i. e.*, their velocity under unit potential gradient) that the specific conductivity of the metal will be UFC, and hence the total resistance of the accelerated conductor will be

$$R_i = \frac{l}{UFCS}. \tag{5}$$

Combining (4) and (5) we obtain

$$\frac{uF}{U} = \frac{IR_iF}{l}. \tag{6}$$

Substituting (3) and (6) in (2) we obtain

$$mv = \int_0^\infty \left(\frac{IR_eF}{l} + \frac{L_eF}{l}\frac{dI}{dt} + \frac{IR_iF}{l} + ka \right) dt. \tag{7}$$

To carry out the indicated integration we may note since the current I has the value zero both at the start and finish of the process that

$$\int_0^\infty \frac{L_eF}{l}\frac{dI}{dt}\,dt = \frac{L_eF}{l}dI = 0. \tag{8}$$

It is also evident that we may write

$$\int_0^\infty Idt = Q, \tag{9}$$

where Q is the total electricity which passes through the circuit, and also write

$$\int_0^\infty adt = v, \tag{10}$$

since v is the total change in the velocity of the conductor. We obtain

$$mv = \frac{QF}{l}(R_e + R_i) + kv,$$

or solving for the total pulse of electricity and putting $(R_e + R_i) = R$ the total resistance of the circuit we obtain the desired equation

$$Q = \frac{(m - k)vl}{RF}. \qquad (11)$$

This is the equation which we have tested in our experiments and have found the pulse of electricity to depend in the way indicated on the variables, velocity v, length l, and resistance R. We have also calculated from our results the value of $(m - k)$ and found this quantity to be nearly the same as the mass of an electron in free space. We shall consider the significance of this fact in the sequel.

In the next paragraphs we shall present a very complete and detailed description of our experimental apparatus, methods and measurements. We think this necessary so that the reader shall have all the material needed for a critical estimate of the significance of our results. Experiments so difficult as the ones we have undertaken where so many accidental effects have to be eliminated must necessarily be subjected to very careful scrutiny, and although we believe that our work demonstrates the existence of the predicted effect, and indeed gives its magnitude with reasonable accuracy, we nevertheless shall welcome criticisms or suggestions as to improvements.

THE EXPERIMENTAL APPARATUS.

A general view of the rotating apparatus is shown in the reproduction from a photograph, Fig. 2. The rotating wheel carrying the coil of wire to be experimented on is shown at A. It is driven from a *three-phase* $1\frac{1}{2}$-horsepower motor by a belt through a gear and worm enclosed in the case at B. The small shaft C leads to a magneto for measuring speed. The large rectangular coils of wire, D, E, are used in neutralizing the earth's magnetic field and the compensating coil F is connected in series with the rotating coil. Connection with the rotating coil is made through the pair of wires G, which run over a pulley on the ceiling of the room above and are allowed to twist up. They come down again at H.

A description of the individual features of the apparatus will be necessary.

The Frame.—The frame of the apparatus was constructed of 2×4 in. scantling fastened together with brass bolts and erected on 4×6 in. sills which were bolted direct to the concrete floor. Such a construction from non-magnetic materials was found to be absolutely necessary, since an iron frame which was tried was found to change its state of magnetization when jarred by the running of the machine, and this

change in magnetization affected the coil enough to produce very large deflections in our sensitive galvanometer.

The Shaft, Bearings, Gears, etc.—The exclusion of iron from any part of the apparatus near the coil made it necessary to use a Tobin bronze shaft (three fourth inch in diameter), running in brass bearings. This shaft was driven by a three-phase 440-volt $1\frac{1}{2}$-horse-power motor, which was belted to a tight and loose pulley driving the gears in the gear case at *B*, Fig. 2. The shaft was provided with two thrust bearings so that it could be driven in either direction by reversing the motor. The lower thrust bearing was a steel ball under the lower end of the shaft in the gear case, and the upper bearing was an ordinary ball bearing seen in the cut just at the lower end of the bronze shaft. The steel balls in this bearing were the nearest iron to the coil and their motion did not affect the galvanometer. It was found necessary, however, to use bronze instead of steel washers in these bearings.

The gears and gear case were those belonging to a "Babcock Standard Milk Tester" and stepped up the speed in the ratio of 3 to 29. It was found necessary to arrange the gear case so that the gears were always immersed in a mixture of oil and oil-dag and even then it was necessary to replace the gears at rather frequent intervals.

The handle for applying the brake is shown at *I*.

The Magneto.—To determine the instantaneous speed of rotation at the time of stopping, the apparatus was made to drive a magneto connected to the shaft *C*. This magneto was set at a considerable distance from the rest of the apparatus so as to avoid possible magnetic disturbances. The voltage of the magneto was found to be very closely proportional to the speed according to the relation 1 centivolt = 0.728 rev. per second of the rotating coil. This voltage was read on a voltmeter conveniently placed. In cheap magnetos such as the one we used there is often considerable fluctuation of voltage owing to poor contact of the brushes. This was pretty well avoided, however, by the use of two pairs of brushes instead of two single brushes. Each pair consisted of a wire brush and a carbon brush, the wire brush of one pair being placed opposite the carbon brush of the other pair, to act as a cleaner. It was also found desirable for steady voltages to arrange a spring to prevent longitudinal motion of the armature with reference to the magnetic field.

The Rotating Wheel.—The most significant part of the apparatus is of course the rotating wheel which carries the coil of wire to be experimented on. A reproduction of this wheel is shown in the accompanying cut, Fig. 3. The coil of wire was wound in the groove *A* which has a depth of one inch and width of fifteen sixteenths inch. The ends of the

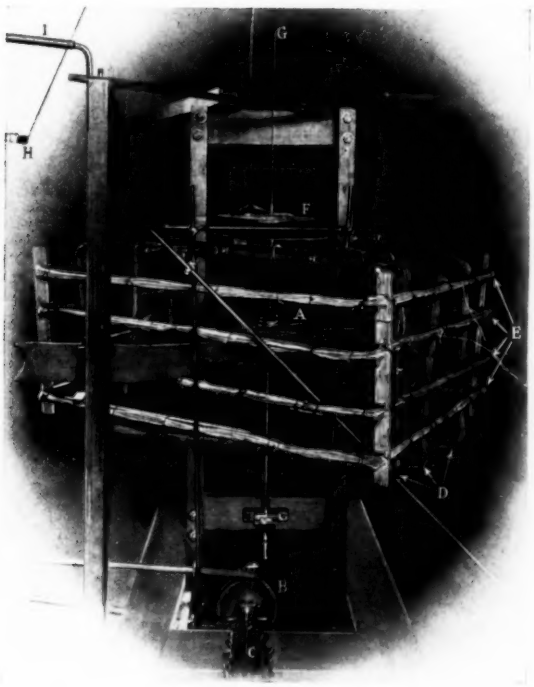


FIG. 2.

FIG. 3.

TOLMAN AND STEWART.

wire were brought to binding posts set on the vulcanite slab *B*. These binding posts were of copper to help in the elimination of thermoelectric effects. The wire used was No. 20 double silk insulated copper wire carefully wound in the lathe, the successive layers being impregnated with parafin. The outside of the coil was protected by two layers of unconnected wire. The length of the wire was measured by resistance and by weight, comparing with fifty-foot samples taken from each end of the wire used, the two methods checking closely. The coil used was 46,650 cm. long and had an average diameter of 24.65 cm. Some of the wire was later removed and experiments made with a shorter coil, 30,370 cm. long with an average diameter of 24.1 cm.

The disk for the wheel was made by gluing together under extremely high pressure a number of layers of birch veneer, each one eighth inch thick, the direction of the grain being changed by 45 degrees in successive layers. Wood was chosen not only because of its high ratio of strength to density which is of course essential, in apparatus subjected to centrifugal action, but also because in experiments made with an aluminum alloy wheel, after stopping the wheel, we obtained, on releasing the brake strap, for some reason which we have not thoroughly investigated an extra pulse of electricity through the galvanometer. Using a wooden wheel we had no such trouble. In the case of metal wheels we were also afraid that currents generated in the wheel itself might make trouble for us by inducing currents in the coil.

The brake strap of heavy leather belting was arranged to pull tight around the circumference of the wheel at *C*, Fig. 3, it being of course desirable from a mechanical point of view to apply the force for stopping the wheel as near as possible to the coil of wire with its large momentum. The strap was arranged to pull as uniformly as possible on the whole circumference to prevent pulling the wheel out of line. It was found possible to stop the machine in a fraction of a second from 5,000 r.p.m.

The Twisting Wires.—One of the most important problems which had to be solved was the matter of making connection with the rotating apparatus, since these connections themselves must not introduce appreciable electromotive forces into the circuit. We finally found that small wires which were allowed to twist up were quite satisfactory. These wires went from the center of the wheel over a pulley on the ceiling of the room above and were kept taut by a small weight. This great length permitted us to make a number of runs without changing the wire. We found No. 28 to be a good size of wire to use and this was either doubly or triply silk insulated. The insulation had to be wound in such a direction as to loosen up on twisting, as otherwise the wire kinked badly. For this reason we had to use different wire in running forward and backward.

By running the machine with these twisting wires short circuited we found that their twisting introduced no appreciable electromotive forces into the circuit. We also found by testing the twisted wires after running that the insulation between the two wires remained perfectly satisfactory.

All of the electric connections were shielded from accidental leaks by White's method of mounting insulators on metal plates which are all connected together.

The Galvanometer.—The galvanometer was an extraordinarily satisfactory d'Arsonval type designed by Dr. Frank Wenner and loaned to us by the Bureau of Standards, and we wish here also to express to Dr. Wenner our deep appreciation of his courtesy in this matter. The initial high sensitiveness of the galvanometer was increased by using a very long optical path. The filaments of a 100-watt concentrated filament tungsten lamp were brought to focus by a two thirds inch objective of an ordinary microscope about 60 cm. from the concave mirror of the galvanometer, which in turn produced a new image of the filaments on a paper scale at a distance of about 10 meters.

The galvanometer was adjusted by its gravity control to have a period of about 10 seconds and was used ballistically. It was standardized with a standard solenoid and found to have with our optical path a sensitiveness of about 4.75×10^{-10} coulombs per millimeter throw, the resistance in the circuit being that actually used, 40 ohms. The sensitiveness varied slightly from day to day and was always redetermined for each set of runs, using the same resistance in the circuit as that used in the actual measurements. The standard solenoid was of such a capacity that we could conveniently use one milliampere as the current to be broken in the primary and this was measured with a Leeds and Northrup milliameter. One milliampere broken in the primary gave a throw of about 45 millimeters on the galvanometer scale. The deflections actually measured were in the neighborhood of 5 to 10 millimeters, but as nearly as we could make out the throw was proportional to the number of coulombs in the pulse of electricity. The standard solenoid was of our own construction and was standardized both by computation and by comparison with a known solenoid lent by the Physics Department of this university, the two methods leading to a satisfactory check.

The Compensating Coil.—With our sensitive galvanometer connected in series with our coil we found that there are rapid fluctuations in the earth's magnetic field which produced continual deflections of the galvanometer up to magnitudes of ten centimeters or more, which were of course enormously larger than the deflection we were going to measure.

This difficulty was overcome by connecting in series with our rotating coil a stationary "compensating coil" having the same magnetic power but wound in the opposite direction. This coil was placed directly over the rotating coil as shown in Fig. 2 at *F*. This coil had to be very carefully adjusted as to length and then almost completely neutralized the bad effects, although sometimes an automobile going rapidly past the corner of the laboratory would produce enough magnetic disturbance to give a deflection of several millimeters.

We do not know whether the continual variation in the earth's magnetic field which we observed is due to the proximity of the city of Berkeley with a probable leakage of stray and variable currents through the earth or whether the phenomenon would be observed anywhere on the surface of the earth. The fact that we got nearly as good compensation, except for such local disturbances as automobiles, when the coils were several feet apart as when they were near together indicates that the sources of the disturbance are at a considerable distance. The subject would be an extremely interesting one for further research.[1]

The Horizontal Anti-Earth Coils.—Not only does the varying part of the earth's magnetic field produce difficulties for experiments of this kind, but the steady horizontal component of the earth's magnetic field must also be neutralized, since otherwise the slight tippings of the wheel during rotation and on application of the brake, even though they are too small to be easily observable visually, are nevertheless sufficient to make the coil of wire cut enough horizontal lines of force to produce enormous deflections of the galvanometer. For this reason we arranged parallel to the horizontal component of the earth's field three rectangular coils of wire shown at *D* in Fig. 1, through which we passed a steady current of the right magnitude to neutralize the component in question. This current was arranged to run through all three coils, a shunt making the current somewhat weaker in the middle coil. The current had to be carefully controlled and also the axis of the coils adjusted with extreme care as to direction. We obtained in this way very good neutralization which was tested by loosening the wheel so that it could be tipped with a motion of about a quarter of an inch at the circumference. With the best adjustment the resulting deflections of the galvanometer were reduced almost to zero. It was found necessary to readjust the direction of the axis and the strength of the current employed at rather frequent intervals, since sometimes even within a day or two we seemed to find small but appreciable variations in the direction or magnitude of the horizontal component.

[1] A considerable amount of work has already been done in this field. See Ebert, J., Terres. Mag. and Atm. Elec., *12*, 1 (1907).

The Vertical Anti-Earth Coils.—After neutralizing the variable part of the earth's field with the compensating coil and the steady horizontal component with the "horizontal anti-earth coils" it was possible to obtain quite reproducible results in our runs, and indeed we collected data for a number of months before we realized that the steady vertical component of the earth's field was leading to a constant error in our measurements. This error arises from the fact that on stopping the machine the centrifugal force which has been acting on the coil ceases and the coil suddenly decreases very slightly in diameter, thus diminishing the vertical flux through the coil by an amount large enough to give a throw of the same order of magnitude as that which we were after, say 10 mm. The possibility of this effect which had entirely escaped our attention was suggested to us by Professor Bridgman, of Harvard University, and we desire to express to him also in this place our grateful acknowledgment.

To do away with this error a set of four rectangular coils were arranged around the wheel on a vertical axis (see *E*, Fig. 1) and a steady current sent through them. The magnitude of the current was regulated well enough so that the earth's vertical field was cut down to about one per cent. of its value in the room outside the coils. This was tested by observing the deflections of a galvanometer placed in series with a small coil of wire held horizontally and arranged so that its area could be suddenly changed. Cutting the field down to one per cent. of its value was quite sufficient to make the error involved negligibly small. We had, moreover, a further test of the efficiency of our arrangement in the fact that with it there were no large or consistent differences in the experimental results obtained when the wheel was run forward or backward, while the centrifugal effect which was present when the earth's field had not been neutralized tended to increase the throw when running in one direction and decrease it when running in the other.

In constructing our apparatus we were most fortunate in being able to rely upon the skill and experience of Mr. G. F. Nelson, the department mechanician, and we wish also here to express our grateful acknowledgment to him.

EXPERIMENTAL PROCEDURE.

In carrying out the actual measurements one of us (T. D. S.) operated the machine, and the other (R. C. T.) observed the galvanometer deflections. The machine was speeded up to the desired point, the belt shifted to the loose pulley, the current thrown off the motor and the motor brought to rest by applying a special brake, thus leaving the apparatus itself the only thing in motion. The observer of the galvanometer then signalled if the galvanometer was reasonably stationary,

the operator applied the brake and read the voltmeter, and the observer noted the galvanometer deflection. It was occasionally necessary to wait a short time before applying the brake because of the temporary presence in the circuit of variable accidental electromotive forces, or because of mechanical vibration of the galvanometer.

The motor operated on three-phase current so that throwing it off and on did not produce serious magnetic disturbances. It was found advisable, however, because of small disturbances produced by the moving armature, to bring the motor to complete rest before trying to measure a deflection.

The galvanometer scale was set at zero just before starting a run, but owing to the introduction of comparatively constant thermoelectric or other electromotive forces incident upon rotation it was usually somewhat off from zero at the instant of stopping. This new rest point, the point of maximum deflection, and the point to which the galvanometer returned, were always recorded.

For convenience we reversed the electrical connections whenever we changed the direction of rotation, thus getting the galvanometer throw always in the same direction.

EXPERIMENTAL RESULTS.

An idea of the kind of results actually obtained is given in Table I., which gives as samples those measurements which were made with the greatest length of copper wire both for forward and backward rotation[1] at speeds in the neighborhood of 80 centivolts as measured on the voltmeter. The variation in individual measurements is fairly large but not more so than might be expected from the nature of the work. The final column gives the number of coulombs passing through the galvanometer divided by the speed of rotation as expressed in centivolts read on the voltmeter which was connected with the magneto. This should be a constant in accordance with equation (11).

The third column shows that the galvanometer might be several millimeters away from the original zero at the instant of stopping. We think that thermoelectric forces were one of the important causes for this initial deflection. The throw was *always* in the direction predicted on the basis of mobile electrons with a negative charge. The throw was always sharp and distinct except at very low speeds. The return to a final rest-point was not quite so definite as the throw, probably partly owing to the gradual change in thermoelectric forces in the circuit after the machine had been stopped. In calculating the throw we always

[1] By forward rotation we mean anticlockwise rotation of the wheel as looked at from above.

TABLE I.

Sample Readings.

Date.	Speed in Centivolts V.	Galvanometer Readings.			Galv. Throw in Mm.	$\frac{Q \text{ (coulombs} \times 10^{11})}{V \text{ (centivolts)}}$.
		From	To	Back to		
Forward rotation:						
Nov. 23, 1915.....	80	0	+ 6¾	− ½	6¾	3.91
" "	79	+ 5	+11	+ 4	6	3.53
" "	90	− 1	+ 8	− 1½	7	4.64
" "	88	− 1	+ 7	− 1	8	4.22
" "	80	+ 4½	+12	+ 4½	7½	4.35
Nov. 25, 1916.....	89	− ½	+ 6½	+ ½	6	3.70
" "	80	0	+ 4½	0	4½	2.64
" "	89	+ 2	+11	+ ½	9	4.66
" "	89	+ 2½	+ 8¾	+ 2½	6¼	3.24
" "	92	+ 1	+ 7½	+ 1	6½	3.25
					Average	3.81
Backward rotation:						
Dec. 6, 1915.....	77	− 3	+ 2	− 1½	5	3.15
" "	80	− 1½	+ 3½	− 1	5	3.04
" "	80	+ 2¼	+ 7¼	+ 2½	5	3.04
" "	71	− 1½	+ 4½	− ½	6	4.11
Dec. 7, 1915.....	86	− 2½	+ 4¾	+ 2½	7¼	4.09
" "	87	− ½	+ 6	− 1½	7½	3.07
" "	77	− 1¾	+ 3¼	− 1½	5	3.15
Dec. 8, 1915.....	73	+ 5½	+12¼	+ 7	6¾	4.22
" "	75	+ 3½	+ 7	+ 1½	3½	2.21
" "	70	+ 4½	+ 7	+ 2	2½	1.69
" "	88	+10¼	+14½	+ 9½	4¼	2.29
" "	72	+ 2	+ 7	− 3	5	3.29
" "	82	0	+ 6½	0	6½	3.76
" "	70	− 5	0	− 5½	5	3.39
Dec. 9, 1915.....	65	+ ½	+ 6½	+ ½	7	4.48
Dec. 10, 1915.....	87	− 6½	0	− 3½	6½	3.51
" "	82	− 2½	+ 3¼	− 2½	5¾	3.29
" "	83	− 7½	− 1½	− 7½	6	3.39
Average.....	.....	.....	.....	.....	.....	3.28

took the difference between the initial point and maximum deflection, although sometimes we could note that a large displacement of the rest point corresponded to an increased or decreased throw (see for example the third throw on December 8). Owing to the width of the image of the filament and the unsteadiness of the galvanometer it was not possible to estimate the position of the galvanometer nearer than about one half or, under favorable conditions, one quarter of a millimeter.

Provided the wheel were stopped with reasonable quickness we found no effect of the speed of stopping on the magnitude of throw. The period of the galvanometer was about 10 seconds and the time necessary to stop the wheel was a fraction of a second.

It was only very rarely necessary to exclude a run from the record because of some known accident occurring during the trial, such as short circuiting, breaking of the connecting wires, or passage of an automobile, etc. A very few runs were also omitted because of a departure of very unusual magnitude arising from unknown causes.

It will be seen from the averages in the last column of Table I. that the throw under these particular circumstances was likely to be a little larger for forward than for backward running. We do not know the whole reason for this unpleasant phenomenon. We think, however, that it is very likely due to small accidental electromotive forces produced by the motion of the coil relative to the wheel when the wheel is stopped. This is borne out by some experiments which we have since made with aluminum wire where very elaborate precautions in the way of shellacking and thus binding together the successive layers of wire were necessary before we could get satisfactory results both with forward and backward running. It is significant to note, as will be seen from Table II., where forward runs are indicated by the plus and backward by the minus sign, that the accidental effect, whatever it is in the case of the shorter wire, made the backward runs give the larger result. (See Remarks under *Vertical Anti-Earth Coil.*) It should be noted that this accidental effect is only of the same order of magnitude as the errors of observation. The study and, if possible, the elimination of this effect would be very desirable. It is, however, a very difficult problem to tackle.

Variation of Q with Speed.—The most immediate purpose of the experimental work was to test the validity of equation (11),

$$Q = \frac{(m - k)lv}{RF}, \tag{11}$$

for the pulse of electricity sent through the galvanometer on stopping. For this purpose we first made a series of runs with the complete length of copper wire varying the velocity. Equation (11) being true, the number of coulombs Q should be proportional to the velocity of rotation. This is shown by Fig. 4, which is made from the data in the first eight lines of Table II., plotting Q as ordinates against the velocity v as abscissæ. The table includes runs made in both directions, the forward runs being indicated by a plus sign and the backward runs by a negative sign. It will be seen from the plot that Q is very closely proportional to the speed.

The fourth column in Table II. gives the rim velocity of the wheel in centimeters per second for the average diameter of the coil of wire. Each value of Q corresponds to a number of runs made in the neighborhood of

TABLE II.

No. of Runs.	Resistance in Ohms.	Length of Wire in Centimeters.	Velocity in Cm./Sec.	Q Coulombs $\times 10^9$.	$(m-k)\times 10^4$ $O=16$.	$\left(\frac{1}{(m-k)}\right)$ $O=16$.
23	40	46,650	+1,980	1.30	5.43	1840
15	40	46,650	−1,980	1.10	4.61	2170
10	40	46,650	+2,820	1.61	4.72	2120
9	40	46,650	+3,670	2.39	5.38	1860
18	40	46,650	−4,400	2.56	4.83	2070
10	40	46,650	+4,790	3.24	5.58	1790
11	40	46,650	+5,520	3.43	5.15	1940
11	40	46,650	−5,640	3.15	4.63	2160
12	32	30,370	+4,960	2.54	5.21	1920
12	32	30,370	−4,960	3.33	6.84	1460
Total 131					Av. 5.238	Av. 1910

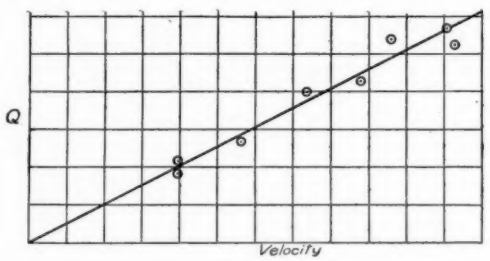


Fig. 4.

this speed, the reduction to a common speed being made by assuming that Q was proportional to the speed over the short range involved.

Variation of Q with Length.—Equation (11) also requires that Q should be proportional to the length of the wire. To test this relation, part of the wire was removed and the runs in the last two lines of Table II. were made. This change in length of wire incidentally changed the total resistance of the circuit from 40 to 32 ohms so that this must also be allowed for on the assumption that Q would be inversely proportional to the total resistance R in the circuit. We obtain from Table II. for the runs with the long wire an average value of 0.522 for the quantity QR/lv and for the runs with the short wire an average value for the same quantity of 0.624 which agree within twenty per cent., which is perhaps as close as could be expected considering the small number of runs made with the short wire.

Calculation of $(m - k)$.—We also used the data in Table II. for the purpose of calculating the value of $(m - k)$ in copper, in accordance with equation (11). The values found are given in the next to the last column and their reciprocals in the last column.[1]

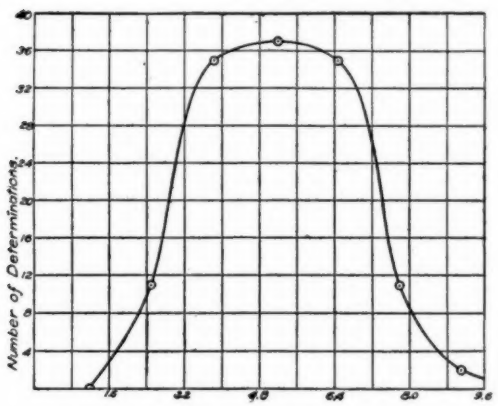
[1] The calculation of $(m - k)$ can be made directly from equation (11) in the form

In order to get an idea of the "probable error" in our determination of $(m - k)$, we given in Table III. a statement of the number of runs which gave values of $(m - k)$ lying within definite equal ranges, thus showing how the individual measurements are distributed about the mean. These results are shown by the plot in Fig. 5, where the abscissæ give the values of $(m - k)$ and the ordinates the number of determinations

TABLE III.

Distributions of Values of $(m - k)$.

No. of Runs.	$(m-k)\times 10^4$ Lying Between
11	184 and 316
35	316 and 448
37	448 and 580
35	580 and 712
11	712 and 844
2	844 and 976



$(m - k) \times 10^4$

Fig. 5.

falling within the small range in question. The highest point of the curve is the mean value for $(m - k)$ and it will be seen that the curve closely resembles the familiar probability curve, indicating that deviations from the mean value are due to indiscriminate accidental effects. The shape of the curve also shows that further measurements with the same appa-

$$(m - k) = \frac{QRF}{lv}$$

provided we substitute all our values in C.G.S. units. Consider for example the calculation of the first value of $(m - k)$ in Table II. We have $Q = 1.30 \times 10^{-10}$ abcoulombs, $R = 40 \times 10^9$ abohms, $F = 9{,}650$ abcoulombs, $l = 46{,}650$ cm., $v = 1{,}980$ cm. per sec.

$$(m - k) = \frac{1.30 \times 10^{-10} \times 40 \times 10^9 \times 9{,}650}{46{,}650 \times 1{,}980} = 5.43 \times 10^{-4} \text{ gm.}$$

ratus would probably not lead to any change in the value of $(m-k)$ greater, say, than $\pm 0.8 \times 10^4$.

DISCUSSION OF RESULTS.

The Value of k.—We have calculated the value of $(m - k)$ from equation (11), which may be written

$$mv = \frac{QRF}{l} + kv. \qquad (11)$$

In this equation mv is the momentum associated with some particular equivalent of electrons situated in the wire, and since these electrons are ultimately brought to rest this momentum is equated to the time integral of the three kinds of forces—"frictional," "electrical" and "accelerational"—which are acting.

QRF/l is the sum of the amounts of momentum destroyed by the "frictional" and "electrical" forces acting on the elctrons, while kv is the momentum destroyed by what we have called the "accelerational" force. Both the "frictional" and the "accelerational" force are exerted by the main body of the wire on the electrons which it contains; the "frictional" force arises because of the motion of the electrons through the body of the wire, while the "accelerational" force arises because of the interaction of the electrons with a body of metal which is itself being accelerated and this force would exist even if the electrons were not lagging behind.

It is difficult to make any estimate as to the value of k. If, however, we assume that the electrons which are doing the conducting are largely present in interatomic spaces which form a relatively large part of the total volume of the metal then we might expect k to be small. And at first sight this might seem to be in agreement with the experimental fact that our value of $(m - k)$, 1/1910, is only slightly smaller than the accepted value for the equivalent mass of slow-moving electrons in free space, *i. e.*, 1/1845.

The Value of m.—In interpreting the results, however, there are modifying effects on the value of m which must also be considered. The mass of an electron is presumably the mass associated with the electromagnetic field which surrounds it. In accordance with the theory of the relativity of motion this mass in grams is equal to the energy of the electromagnetic field in ergs multiplied by the square of the velocity of light, so that the amount of this mass will evidently depend upon the configuration of the field. For a slow-moving electron in free space the lines of force spread out radially and run off to infinity, most of the mass,

however, being located close to the electron itself. For an electron situated in the body of a metal the configuration of the field will be changed. The fact that the lines of force for electrons in a metal no longer run off to infinity will be a factor tending to decrease the electromagnetic mass, such a shortening of the lines of force being accompanied by a decrease in the potential energy of the field. On the other hand there are two important causes which might make the mass of electrons in metals larger than in free space. In the first place, the lines of force from an electron in a metal will not run out radially but will be bunched in the direction of the nearest positive charges, and such a distortion is accompanied by an increase in potential energy and hence an increase in the mass of the system. Part of the mass of such a system, however, might be thought of as belonging to the positive charge. Furthermore, an overlapping of the fields of two electrons can lead to an increase in mass, since at any point the field strengths will be directly additive while the energy density at the point in question will go up as the square of the field strengths.

Owing to these uncertainties as to the values of k and m in metals we cannot for the present draw any definite conclusions from the close correspondence of the mass of an electron in free space and our value for $(m - k)$. The evidence presumably favors the belief that k is small and m not much different from its value in free space, but of this we cannot yet be certain. One natural method of attacking the general problem is to carry out measurements with other metals than copper and see whether $(m - k)$ is always of the same order of magnitude as m in free space. Measurements are now under way on aluminum and silver, and we hope to report on these at a later time. We can already state that the results are in the same direction and of the same order of magnitude as in copper.

On the Nature of the Conducting Process in Metals.—Our purpose in carrying out the measurements that we have described has not been merely to demonstrate an effect which has long been an object of search, we have also had in mind the possibility of obtaining from our experiments information as to the nature of the conducting process in metals and indeed perhaps further information as to the nature of the electron itself.

Equation (11) which we have tested in this article was derived on the assumption that the conducting process in metals is in the nature of a drift of "free" electrons when acted on by an electric field, and the fact that the equation seems to fit the experimental facts is to some extent a verification of these assumptions. Such considerations are of particular interest at the present time in view of Sir J. J. Thomson's proposal[1] of a

[1] Thomson, Phil. Mag., *30*, p. 192, 1915. Richardson, ibid., *30*, p. 295, 1915.

quite different theory of metallic conduction. According to his theory, a metal contains atoms which are in the nature of electrical doublets which will orient themselves parallel to any applied electrical field. These atoms are assumed to have the power of ejecting electrons in the same direction as the axis of the doublet and hence the conducting process on the basis of this theory consists in a tendency for orientation of the doublets under the action of the applied electromotive force and consequent ejection of electrons from one atom to another in the direction which the current is known to flow. It seems very doubtful to us whether such a theory can be satisfactorily brought into agreement with our experimental results, since it would seem at first sight to be merely an accidental coincidence if the *mechanical* forces which we apply should produce an orientation in the right direction and of the right amount to give the pulse of electricity whose magnitude we have calculated on the basis of the other theory and actually found experimentally.

UNIVERSITY OF CALIFORNIA,
February 25, 1916.

COMPTON'S FORMULA FOR THE TEMPERATURE VARIATION OF THE SPECIFIC HEAT OF SOLIDS.

BY F. SCHWERS.

IN a recent article,[1] Arthur H. Compton has made an attempt to establish a new formula for the specific heat curve of solids down to low temperatures. This expression for the atomic heat at constant volume is:

$$C_v = 3NR\, e^{-\frac{\tau}{T}}\left(\frac{\tau}{T} + 1\right),$$

in which $3N$ is the greatest possible number of degrees of freedom, R and T respectively the gas constant and the absolute temperature, and $\tau = \epsilon/2R$, in which ϵ is the critical energy below which a degree of freedom remains agglomerated, the expression "agglomeration" being used in the sense of Benedicks, and referring to any state of association of the atoms on account of which degrees of freedom for thermal motion disappear. Compton claims in favor of his conception (*a*) that it is independent of the "somewhat hypothetical 'quantum' theory" on which are based the previous formulæ (Einstein, Nernst-Lindemann, Debije), (*b*) that it is not so "largely empirical" as Debije's assumption and (*c*) that it is strongly supported by experimental evidence.

Let us for the present only consider this last claim. The experimental verification of his new formula was made by Compton on the following substances: diamond, copper, silver, aluminium, lead, potassium chloride and sodium chloride. In the case of diamond, little is to be said, since the actual values—even at temperatures as high as 80° absol.—are too small and their determination relatively too inaccurate to enable us to state which formula suits better the experimental data. But it appears that in the case of copper, aluminium and lead, Compton has not considered the latest and best available experimental figures, but relatively old ones, which do not go down to the very low temperatures now attained. Let us see in this article to what results we arrive if we consider the most recent values found for those three elements.

Copper.—For copper, Compton considered the series which I reproduce in Table I.; the more specially interesting figures between liquid hydrogen

[1] PHYSICAL REVIEW, 1915, p. 377.

and liquid air temperature were taken from Nernst. With these data, I have calculated from C_v obs. the values of $\beta\nu$ according to Debije's formula.[1] In Column IV. we find the calculated values for C_v with the mean $\beta\nu = 313$; the figures of τ are calculated likewise (Col. V.) and in Column VI. the numbers representing C_v for $\tau = 133.5$ are simply reproduced from Compton's original paper. From 33°.5 upwards (also

TABLE I.

I.	II.	III.	IV.	V.	VI.
T	C_v Obs.	$\beta\nu$ (Debije).	C_v Calc. ($\beta\nu = 313$).	τ (Compton).	C_v Calc. ($\tau = 133.5$).
23°.5	0.22_3	302	0.19_5	130.0	0.14
27°.7	0.32_4	311	0.32	128.5	0.26
33°.4	0.54	317	0.56	134.0	0.56 (0.55)
87	3.36	313	3.36	131.8	3.32 (3.25)
88	3.37	316	3.38	133.0	3.36

for the values above 90° not referred here) both formulæ give a good agreement; it is really difficult to say which should be preferred. Close to the "normal value" (according to Dulong and Petit's law) a strict comparison between Columns IV. and VI. is not possible, because the value chosen for C_∞ is 5,955 in one case (Debije) and 6,081 in the other (Compton). By taking 5,955 also in the last case, the calculated C_v figures would be reduced as shown in two instances (numbers in brackets); but then the comparison becomes somewhat less fair for Compton, inasmuch it is only necessary to calculate with a slightly higher mean τ-value to get a better agreement.

But if we now consider the experiments between 23°.7 and 27°.7, the expression of Debije still holds good, whereas that of Compton gives decidedly too low values. This will appear to a still greater extent if we take into account the recent and most accurate measurements of Keesom and Kamerlingh-Onnes[2] between the temperatures of 15° and 21° abs. The mean value of $\beta\nu$ (Debije) as deduced from those experiments is somewhat higher (323.5) but remains exceedingly regular over the range considered; whereas there is an increase of τ from 104.5 at 15°.24 to 121.2 at 21°.5, which leads to a complete disagreement for C_v calculated with the τ-values found for higher temperatures, *e. g.*, 133.5: at 15°.24, for instance, the calculated value is 5 times smaller than the observed. Thus it appears that in the range where Debije's formula reduced to the simple form $C_v \sim T^3$ agrees remarkably well with the

[1] Annalen der Physik, vol. 39 (1912), p. 802.

[2] Proceedings Amsterdam Academy, 1914, p. 894.

TABLE II.[1]

I.	II.	III.	IV.	V.	VI.
T	C_v Obs.	$\beta\nu$ (Debije).	C_v Calc. ($\beta\nu = 323.5$).	τ (Compton).	C_v Calc. ($\tau = 133.5$).
15°.24	0.0491	322.3	0.0486	104.5	0.0091
17 .50	0.0726	324.9	0.0735	112.1	0.0249
18 .03	0.0792	325.2	0.0804	113.7	0.0304
18 .89	0.0930	322.9	0.0925	115.6	0.0409
19 .58	0.1010	325.6	0.1030	118.0	0.0505
20 .88	0.1247	323.7	0.1249	120.7	0.0727
21 .50$_5$	0.1410	320.0	0.1365	121.2	0.0862

[1] For the calculation according to Debije's formula, I used the table given by Nernst (K. Akad. der Wissentsch., 1912, p. 1125), with $C_\infty = 5{,}955$. For this same value of C_∞, I calculated the figures C_v for given τ/T, according to Compton's formula

$$\frac{C_v}{C_\infty} = e^{-\frac{\tau}{T}}\left(\frac{\tau}{T} + 1\right)$$

and the obtained table has been used except in those cases where quotations are made from Compton's original paper.

experiments, the discrepancy shown by Compton's expression becomes greater. It may be suggested that this remarkable agreement up to $T = 20°$ with Debije's expression does no more hold good at higher temperatures. This is true to a certain extent inasmuch there is a certain variation in the $\beta\nu$-values, which we also notice in the case of other substances. I want to illustrate this by means of the latest

TABLE III.

I.	II.	III.	IV.	V.	VI.
T	C_v Obs.	$\beta\nu$ (Debije).	C_v Calc. ($\beta\nu = 315$).	τ (Compton).	C_v Calc. ($\tau = 133.3$).
14°.51	0.0396	330	0.0453	103.0	0.0060
15 .59$_5$	0.0506	326	0.0567	106.4	0.0109
17 .17	0.0687	325	0.0750	111.1	0.0222
20 .19$_5$	0.1155	321	0.1210	119.5	0.0616
20 .74$_5$	0.1217	324	0.1313	120.5	0.0714
25 .37	0.234	319	0.243	127.7	0.194
29 .73	0.377	317	0.406	132.6	0.369
40 .22	0.870	315	0.870	137.0	0.934
50 .04	1.434	315	1.434	137.3	1.520
59 .75	2.06	310.5	2.02	133.5	2.065
60 .33	2.08	312	2.05	133.3	2.08
69 .66	2.58	313	2.57	132.4	2.56
80 .32	3.04	317	3.07	131.4	3.00
88 .86	3.35	321	3.41	132.0	3.32
89 .38	3.42	316.5	3.43	129.6	3.34

experiences of Keesom and Kamerlingh-Onnes[1] ranging from 14° to 90°. The $\beta\nu$-value calculated with (Column IV., Table III.) is lower than previously (315) and is the mean of those actually deduced from the experiments above 29°.73 (Column III.). For the same conditions, we find the mean value of $\tau = 133.3$. The conclusion to be drawn is that, even for simple monoatomic metals, like copper, the ideal formula has not yet been found, but that Compton's expression certainly does not bring us nearer towards this achievement.

I proceed now to show that the behavior of aluminium and lead confirm what has just been said about copper.

ALUMINIUM.

Table IV. reproduces the data quoted by Compton to which I have added the comparison with the values calculated according to Debije. There again, Compton's formula gives somewhat low results at 32°.4

TABLE IV.

I.	II.	III.	IV.	V.	VI.
T	C_v Obs.	$\beta\nu$ (Debije).	C_v Calc. ($\beta\nu = 395$).	τ (Compton).	C_v Calc. ($\tau = 169.6$).
32°.4	0.25	398	0.25_5	160.1	0.19
35 .1	0.33	392	0.32_0	162.3	0.28
83 .0	2.40	393	2.39	169.6	2.40 (2.35)
86 .0	2.51	395	2.51	169.6	2.51
88 .3	2.61	395	2.61	169.0	2.60 (2.55)

and 35°.1, but for the rest of the curve, the calculated atomic heats fit the curve well, although there is no "closer agreement" than with

TABLE V.

I.	II.	III.	IV.	V.	VI.
T	C_v Obs.	$\beta\nu$ (Debije).	C_v Calc. ($\beta\nu = 382$).	(τ Compton).	C_v Calc. ($\tau = 164.0$).
19°.1	0.066	365	0.058	124.3	0.010
23 .6	0.110	381	0.109	140.0	0.045
27 .2	0.162	386	0.166	148.9	0.101
33 .5	0.301	386	0.310	158.5	0.260
37 .1	0.396	386	0.409	163.2	0.390
41 .9	0.597	386	0.613	162.8	0.586
49 .6	0.901	383	0.907	166.7	0.939
53 .4	1.105	379	1.084	166.2	1.126
62 .4	1.543	379	1.520	165.0	1.561
73 .4	2.070	379	2.060	163.5	2.077
79 .1	2.345	380	2.326	161.9	2.303

mean: 164.0

[1] Proceedings Amsterdam Academy, 1915, p. 484.

Debije's formula. The defect of Compton's expression appears again at the lower temperatures which were reached in experiments carried out by Nernst and myself[1] (Table V.). The mean value of $\beta\nu$ employed is somewhat smaller (382 instead of 395), but it is the mean of the actually found values (Column III.) and this small difference hardly affects the C_v calc. for higher temperatures.

But again, τ is very much lower between 19°.1 and 33°.5 and gives only a certain degree of constancy above 37°.1, its mean being $\tau = 164.0$. I calculated C_v with this τ-value, which gives a fairer chance for Compton's formula than the previously adopted value (169.6): in spite of that, a great discrepancy is to be seen at the very low temperatures, and at 19°.1, the calculated value is nearly 7 times smaller than the observed one.

LEAD.

Here also I reproduce for sake of comparison, the table given by Compton with addition of the figures calculated from Debije's formula (Table VI.). I desire to point out that the value found at 28°.3, *e. g.*,

TABLE VI.

I.	II.	III.	IV.	V.	VI.
T	C_v Obs.	$\beta\nu$ (Debije).	C_v Calc. ($\beta\nu = 94$).	τ (Compton).	C_v Calc. ($\tau = 38.4$).
23°.0	2.95	93.2	2.92	39.5	3.04 (2.995)
28 .3	3.91	—	3.63	—	3.69
36 .8	4.38	94.2	4.38	38.4	4.38
38 .1	4.43	95.5	4.47	38.7	4.45 (4.37)
85 .5	5.57	98.9	5.61	39.9	5.60 (5.50)
90 .2	5.63	96.2	5.65	40.6	5.67 (5.54)

3.91, is certainly too high (disagreement for both formulæ). As regards the general agreement, we can say that it is of the same order for the two expressions.

I shall now consider the experiments of Eucken and myself,[2] which were carried out under conditions of great accuracy. Instead of the rather high value of $\beta\nu$ (94), these figures agree exactly with the lower value 88. The agreement is certainly much better than with Compton's formula, which gives a variation of τ from 38 to 30. Calculating with the mean value, *e. g.*, 34.7, we arrive in all cases at figures showing rather big differences with the observations: up to $T = 30°$, the values are too high and further up, they are too low, and at no part do they agree

[1] Berl. Akademie Stzber., 1914, p. 369.

[2] Ber. deutsch. phys. Gesellsch., 1913, p. 578.

TABLE VII.

I.	II.	III.	IV.	V.	VI.
T	C_v Obs.	$\beta\nu$ (Debije).	C_v Calc. ($\beta\nu = 88$).	τ (Compton).	C_v Calc. ($\tau = 34.2$.
15°.98	1.87	88.0	1.87	37.9	2.20
18 .90	2.35	90.8	2.47	38.7	2.74
21 .22	2.76	91.0	2.88	38.2	3.11
22 .4	3.00	89.6	3.06	37.4	3.26
23 .52	3.16	90.0	3.23	37.2	3.41
25 .53	3.50	88.1	3.50	36.0	3.65
27 .55	3.68	90.0	3.74	36.5	3.85
30 .24	4.06	87.1	4.03	34.6	4.10
31 .3	4.12	88.4	4.13	35.1	4.18
33 .55	4.33	87.5	4.32	34.4	4.34
40 .0	4.72	88.3	4.73	33.7	4.70
40 .4	4.79	86.0	4.76	34.0	4.72
47 .2	5.08	85.0	5.03	31.8	4.97
47 .6	5.07	86.0	5.04	31.8	4.99
49 .74	5.13	87.0	5.11	32.3	5.05
50 .9	5.18	86.5	5.15	31.7	5.08
54 .5	5.26	87.2	5.25	32.0	5.17
83 .13	5.64	87.3	5.63	29.5	5.57
86 .23	5.65	89.0	5.66	30.1	5.59
88 .9	5.66	90.4	5.67	30.5	5.61

better than those calculated with Debije's formula. Thus even in this case, where the atomic heat does not fall down to the very low values observed for copper and aluminium, we can by no means say that Compton's formula is an improvement: it is exactly the contrary.

Still, as in the case of copper, it must be agreed that Debije's formula does not always entirely fit the experimental curve and that discrepancies occur which certainly exceed the experimental errors. This again means, that in the case of lead also, we can only get approximate values if we calculate over the whole range with a single value of $\beta\nu$. But this does not alter the fact that Compton's formula fits much less closely.

For the sake of completeness, I desire to refer also to the quite recent data of Keesom and Kamerlingh-Onnes.[1] These authors have made three sets of experiments between 14° and 20° of which only the last one is given here, together with the determinations made up to 70° (Table VIII.). Between 14° and 20°, the values of $\beta\nu$ and of τ are very constant, the last ones being respectively for the three series 38.0, 37.5 and 37.2. But at higher temperatures, *e. g.*, over 30°, τ decreases gradually and reaches low values, coming down to about 32 at 60°. Truly, there are in this set some discrepant figures, which I put in brackets: by plotting

[1] Proceedings Amsterd. Academy, 1914, p. 894.

TABLE VIII.

I.	II.	III.	IV.	V.	VI.
T	C_v Obs.	$\beta\nu$ (Debije).	C_v Calc. ($\beta\nu = 88$).	τ (Compton).	C_v Calc. ($\tau = 36.5$).
14°.19	1.56	85.7	1.48	37.3	1.63
15 .31$_5$	1.81$_5$	85.9	1.74	37.0	1.86
16 .27$_5$	1.99	86.6	1.94	37.2	2.05
17 .24	2.17	86.9	2.13	37.2	2.23
18 .25$_5$	2.41	86.3	2.34	36.6	2.42
19 .27	2.53	88.2	2.54	37.2	2.60
20 .30$_5$	2.66	89.5	2.72	37.6	2.76
22 .31	2.97	89.9	3.05	37.5	3.06
27 .51	3.59	92.4	3.74	37.6	3.68
28 .50	3.65	94.0	3.85	38.2	3.78
36 .49$_5$	4.45	90.5	4.53	35.4	4.38
(45.61$_5$)	(4.81)	—	—	—	—
46 .25	5.00	87.9	5.00	33.4	4.84
(57 .20)	(5.38)	—	—	—	—
58 .00	5.32	88.5	5.32	31.9	5.17
(69 .28)	(5.31)	—	—	—	—
(69 .97)	(5.34)	—	—	—	—

the observations on a diagram, those values (at 45.62, 57.20, 69.28 and 69.97) are situated somewhat outside the general curve. The authors too refer to those discrepancies as due to some experimental errors, and disregarded them for the comparison with Debije's formula; the other values correspond most exactly with the figures of Eucken and myself, the same value of $\beta\nu$ (88) being also adopted by Keesom and Kamerlingh-Onnes. Incidentally, it may be remembered that the experiments are more difficult—ceteris paribus—at these higher temperatures: the Dewar vessel contains liquid hydrogen, thus never reaches more than 20°.4 during the whole set of experiments. The more the temperature of the examined substance is raised by successive heatings, the greater becomes the danger that small defects of the vacuum may bring about irregular temperature interchanges which naturally affect the results. On the other hand, the three sets of Keesom and Kamerlingh-Onnes below 20° are most remarkable; their agreement with the results of Eucken and myself are closer than could be expected. Thus we are quite safe in disregarding those four somewhat doubtful results. In order to be quite fair to Compton, I calculated with the mean value of τ, which is in this case 36.5. Here again, it will be seen that, on the whole, Debije's formula agrees better than Compton's (Table VIII.).

The expression deduced by Debije as first approximation for the case of regular monoatomic substances, is reduced to the simple law of a

proportionality between C_v and T^3 below a certain value of $\beta\nu/T$. This must also be true under certain restrictions for regular polyatomic substances and it has been experimentally verified in the case of fluorite CaF_2 and pyritis FeS_2 in the already quoted paper of Eucken and myself. Let us see to what results we arrive if we compare Compton's formula with the results given by that of Debije. Here, C_v represents the mean atomic heat, *e. g.*, the molecular heat divided by 3, both CaF_2 and FeS_2 having three atoms in the molecule. The last column is the

TABLE IX.

I.	II.	III.	IV.	V.		VI.
T	$C_v\left(\frac{\text{Mol. Heat}}{3}\right)$.	$\beta\nu$ (Debije).	C_v Calc. ($\beta\nu = 474$).	τ (Compton).		C_v Calc. ($\tau = 206$).
17°.5	0.0213	483	0.0233	136.6		0.0010
19 .9	0.0343	475	0.0344	144.7		0.0024
21 .5	0.0439	473	0.0434	150.2		0.0045
23 .5$_4$	0.0560	476	0.0570	158.0		0.0092
25 .6	0.0727	476	0.0733	164.0		0.0173
27 .6	0.092	475	0.0756	169.3		0.0288
29 .1$_5$	0.110	471	0.108	172.9		0.0408
34 .0	0.179	467	0.172	182.1		0.0946
36 .8	0.221	470	0.217	187.8		0.146
37 .5	0.238	469	0.230	188.0		0.160
39 .8	0.279	471	0.275	192.0		0.206
42 .0	0.329	469	0.319	194.0		0.261
45 .2	0.407	465	0.389	197.3		0.346
47 .9	0.463	476	0.469	201.4		0.428
50 .3	0.531	480	0.556	203.0		0.505
52 .6	0.608	481	0.634	203.2		0.583
55 .1	0.680	483	0.712	205.0		0.670
57 .4	0.751	481	0.778	206.4		0.755
59 .6	0.823	479	0.842	207.3		0.837
66 .5	1.102	472	1.092	206.0	Mean: 206.0	1.102
67 .9	1.155	474	1.155	206.1		1.152
69 .7	1.198	477$_5$	1.220	207.7		1.212
81 .6	1.681	475	1.693	206.0		1.681
82 .1$_5$	1.694	477	1.720	206.5		1.702
82 .7	1.724	476	1.740	205.9		1.723
83 .9	1.754	479	1.790	206.9		1.767
86 .0	1.846	477	1.870	206.0		1.846

atomic heat calculated with the mean value of τ considered from the moment that τ becomes constant. In the case of CaF_2 (Table IX.), this value is $\tau = 206$, and the constancy only starts at about 50°; for the lowest temperature considered, *e. g.*, 17°.5, τ is only = 136.6, and the calculated value, with $\tau = 206$, is 20 times smaller than the observed

figure. In the case of FeS_2 (Table X.), there are some discrepancies with Debije's formula, about which there are a few remarks in the paper referred to; but this disagreement below 26°.6 and over 66°.1 is only very small compared with the large differences given by Compton's formula: with $\tau = 268$—which is the mean from 57° upwards—we arrive

TABLE X.

I.	II.	III.	IV.	V.	VI.
T	$C_v\left(\frac{\text{Mol. Heat}}{3}\right)$.	$\beta\nu$ (Debije).	C_v Calc. ($\beta\nu = 645$).	τ (Compton).	C_v Calc. ($\tau = 268$).
21°.7	0.0216	604	0.018	169	0.0004
23 .1	0.0251	612	0.021	176	0.0008
24 .3	0.0288	614	0.025	181	0.001
25 .1	0.0319	613	0.027	185	0.002
26 .6	0.0362	638	0.033	192	0.003
27 .5	0.0366	642	0.0360	198	0.004
27 .8	0.0377	643	0.0372	199	0.005
29 .8	0.0462	644	0.0458	206	0.007
29 .9	0.0467	644	0.0463	207	0.007
30 .3	0.0467	652	0.0483	209	0.009
32 .9	0.0597	652	0.0617	218	0.016
33 .4	0.0617	655	0.0645	220	0.018
35 .8	0.077	651	0.085	227	0.028
37 .0	0.087	647_5	0.088	229	0.035
38 .3	0.098	643	0.094	232	0.044
42 .2	0.134	639	0.130	240	0.076
46 .7	0.179	642	0.176	250	0.129
49 .0	0.207	640	0.204	254	0.163
51 .7	0.237	648	0.236	260	0.207
54 .3	0.281	642	0.277	261	0.255
56 .9	0.317	646	0.319	266	0.306
66 .1	0.547	626	0.494	264	0.523
68 .0	0.587	630	0.545	266	0.573
70 .4	0.637	634	0.606	268	0.637
72 .6	0.697	630	0.659	268	0.697
75 .4	0.767	627	0.722	269	0.776
81 .4	0.900	629	0.841	274	0.954
82 .4	0.973	616	0.872	269	0.985
84 .0	1.037	612	0.913	268	1.037

Mean: 268

at 21°.7 at a C_v calc. which is 50 times smaller than the observed value. The choice of smaller τ-values for the calculation would have given smaller differences at low temperatures and larger differences at higher temperatures, but would not have altered the fact that in the case of the polyatomic substances also, Compton's formula does not agree with experiment.

Without entering into the details of Compton's "agglomeration"

hypothesis or of his calculations, it may suffice to say that his final formula

$$\frac{C_v}{C_\infty} = e^{-\frac{\tau}{T}}\left(\frac{\tau}{T} + 1\right)$$

must immediately arouse suspicion. Einstein's purely theoretical formula gave much too low results at low temperatures and the corrective term added by Nernst and Lindemann, although giving, on the whole, a much better agreement, possesses also the defect of giving too rapidly decreasing values towards the absolute zero: the changes in this region are proportional to T^3 and are not as rapid as is assumed by an exponential formula of any kind. Nernst-Lindemann's expression has been a very good "working" formula, but Debije's considerations constitute a great step in advance, whatever may be the amount of empiricism and rough approximation with which they are still affected.

Compton's formula might also be considered as a "working" formula, of the same kind as that of Nernst and Lindemann, but not even as good as the last named, as will be seen by the example of copper for the range between 15° and 22°, already examined previously, in Table II. The calculated values are to be found in Column IV., Table XI., for $\beta\nu = 321$,

TABLE XI.

I.	II.	III.	IV.	V.
T	C_v Obs.	Debije ($\beta\nu = 323.5$).	Nernst-Lindemann ($\beta\nu = 321$).	Compton ($\tau = 133.5$).
15°.24	0.0491	0.0486	0.009	0.009
17 .50	0.0726	0.0735	0.027	0.025
18 .03	0.0792	0.0804	0.033	0.030
18 .89	0.0930	0.0925	0.044	0.041
19 .58	0.1010	0.1030	0.056	0.051
20 .88	0.1247	0.1249	0.080	0.073
21 .50$_5$	0.1410	0.1365	0.095	0.086

and are to be compared with those calculated for $\beta\nu = 323.5$ (Debije) and $\tau = 133.5$ (Compton). A glance at the table renders any further consideration unnecessary.

The fact that Compton's formula is deduced without any "quantum hypothesis" is certainly interesting in itself; but the formula is a decided failure, so far as the experimental data is concerned, which is, after all, of major importance.

There have been recently many attempts to establish a theory of radiation for the solid state without the help of Planck's "quanta." In this respect, I only want to quote a few papers: the deductions of

Byck,[1] based upon non-euclidean geometry; Callendar's specific heat theory;[2] Brillouin's mathematical suggestions;[3] Tolman's considerations about the "principle of similitude"[4] and Ratnowsky's deduction of Planck-Einstein's energy formula.[5]

Whether the quantum theory, in its present or in a modified form will remain in future, may be said to be for the moment a simple matter of opinion, though I think it becomes more and more difficult to do without this hypothesis. At any rate this theory has nothing which hurts our old physical conceptions: the supposition that energy should be evolved or absorbed by definite quantities only is after all not more extraordinary than the hypothesis that matter is only taken in or given out in definite quantities, *e. g.*, atoms.

What we now require in respect of the atomic- or molecular-heat theory, is a conception, with or without quanta, which will apply not only to simple monoatomic or regular substances, but also to complex compounds of all kind and to substances showing absorption.

UNIVERSITY COLLEGE, LONDON.

[1] Annalen der Physik, *42*, 1913, p. 1417.
[2] Philos. Magaz., 26, 1913, p. 787 and 27, 1914, p. 870.
[3] Annales de physique, 1914, p. 13, p. 163 and p. 433.
[4] PHYSICAL REVIEW, III., 1914, p. 244.
[5] Ber. d. deutsch. phys. Ges., 1915, p. 64.

ON THE ELECTROSTATIC MEASUREMENTS OF ELECTRODE POTENTIALS.

BY G. BORELIUS.

IN 1913 the present writer[1] made a first electrostatic measurement of electrode potentials. This investigation seemed to give the very surprising result that the electrode potentials, thus measured on single electrodes, were not to be reconciled with the theory of Nernst. Using another electrostatic method Arthur W. Ewell[2] was recently led to the same view. Ewell also supposes his method to give new absolute values for the electrode potentials. However the writer's further investigations have shown these earlier results to be surely due to an inaccurate opinion about the phenomena at the wall of the vessel containing the solutions. This I have also pointed out in two later papers[3] containing a closer examination of these very boundary potentials. On account of Ewell's paper, and especially as some of my earlier results are only published in the Swedish language, an analysis of the subject here may be in place.

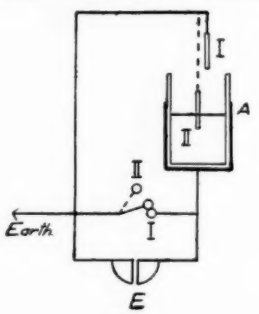


Fig. 1.
Method of Ewell.

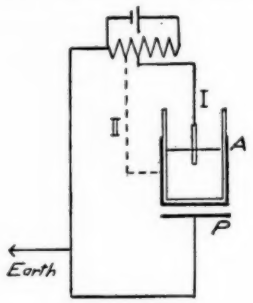


Fig. 2.
Method of Borelius.

The writer has also made some new experiments in order to get a more direct comparison with Ewell's measurements.

To begin with, a short description of our two methods, as I now understand them, will show, I think, that there is no essential difference between their results. The figure gives a schematic sketch.

[1] Ann. d. Physik, 42, 1129, 1913.

[2] PHYS. REV., New Series, 6, 271, 1915.

[3] Ann. d. Physik, 45, 929, 1914. Lunds Universitat Årsskift, 11 (5), 1915.

By Ewell's method the electrolyte is contained in a flask or beaker *A* of glass or quartz, the outside of which is coated with a thin film of silver or aluminum. At first (Case I.) this film is earthed for several hours. After such a long time, in spite of the very low conductivity of the glass (or quartz), the electrolyte must reach a potential such that there is no field of electrical force in the glass. The earth's potential being zero, the potential throughout the glass may then be represented by the notation:

[glass—metal film]. (1)

Then (Case II.) the film is disconnected from earth, the earthed electrode is dipped into the electrolyte, and the accompanying change in the film potential observed at an electrometer *E*. The potential of the glass just at the inside of the vessel in this case becomes:

[electrolyte—electrode] + [glass—electrolyte]. (2)

The deflection of the electrometer (by a special calculation transformed into volts) then becomes proportional to the sum of potential differences: (2)-(1) or

[electrolyte—electrode] + [glass—electrolyte] + [metal film —glass]. (3)

By the writer's method the electrode, which is kept permanently in the electrolyte, is connected to earth over a measured compensation potential. In the earlier experiments the outside of the vessel *A* containing the solution was bare (that is certainly covered with a thin, moist and slightly conductive surface layer); in the later ones it was coated with a film of silver to give more constant conditions. Opposite this film moves an earthed copper plate *P*. The compensation potential is so adjusted as to make the field of electrical force between the surfaces of the vessel and the copper plate zero. The disappearance of this field is shown by means of a special manipulation. Taking the sum of potential differences all round we get for a glass vessel:

[electrolyte—electrode] + [glass—electrolyte] + [surface film—glass] + [air—surface film] + [copper—air] = compensation potential. (4)

The writer thus measures the sum of five potential differences against Ewell's three. Two of them however if necessary, when the surface film is metallic, may easily be eliminated by connecting the film directly with the compensation apparatus (case II. in fig.). Thus we get

[air—metal film] + [copper—air] = compensation potential. (5)

(5) subtracted from (4) gives

[electrolyte—electrode] + [glass—electrolyte] + [metal film—glass]
= a difference of compensation potentials. (6)

The measured circuits are the same in (3) and (6).

In this manner the writer has made the following measurements to compare with those of Ewell. Using a vessel of glass, outside coated with a film of silver, I get for the circuits.

$$^{-}\text{Ag} - n/1\ \text{AgNO}_3\text{—glass—silver film}^{+}$$

¼ hour after filling the vessel	+ 0.375 volt,
3 hours later	+ 0.365 "
10 hours later	+ 0.365 "

Ewell gets as a mean for several vessels of glass and quartz coated with films of silver and aluminum for the same circuit + 0.50 ± 0.03 volt. Taking means for each combination separately we get from his measurements values such as 0.38 ± 0.01, 0.41 ± 0.02, 0.67 ± 0.02, 0.80 ± 0.19, etc. Indeed the values of means and mean errors are such as would be supposed, if judged by common probability calculations, to belong to measurements on different phenomena. The writer's result agrees with Ewell's lower values. The two methods thus are surely equivalent.

We next pass on to the question of the interpretation of the results obtained from electrostatic measurements. In his first paper on this subject the writer supposed all the terms in (4) except the electrode potential to be constant, independently of the kind and the concentration of the solutions. All observed variations in the compensation potential were thus brought back upon the electrode potential. The correctness of this supposition of constancy, at least for a short time, is, moreover, evident as to all the differences except that between glass and solution. About this I have later entirely changed my opinion.

Ewell in his assumptions goes much further than the writer ever did. He puts the potentials

$$[\text{glass—metal}] = 0 \quad \text{and} \quad [\text{glass—electrolyte}] = 0 \tag{7}$$

and in this manner he gets from (3)

$$[\text{electrolyte—electrode}] = \text{measured potential} \tag{8}$$

and thus assumes his method to be an absolute one. The assumptions (7) however are not proved by Ewell's measurements. The only thing proved is that the measured potential differences do not vary more than about one tenth of a volt when solutions, vessels and metal films are altered. But also this limit, I think, could easily have been passed if the variations had only been effective enough.

In fact in the writer's own measurements there are to be seen several examples of much greater variations. The following examples will show that the potential at the surface is considerably different for different insulators and electrolytes. I have found:

$$[\text{glass}—n/2\ \text{HCl}] - [\text{glass} - n/2\ \text{KOH}] = +0.620 \text{ volt},$$

$$[\text{quartz}—n/2\ \text{HCl}] + [\text{quartz}—n/2\ \text{NaOH}] = +0.35 \text{ volt},$$

$$[\text{paraffin}—n/2\ \text{HCl}] - [\text{paraffin} - n/2\ \text{KOH}]^2 + 0.036 \text{ volt}.$$

The solutions were connected with a calomel normal electrode and the liquid potentials calculated by a formula of Henderson.[1] The glass beaker used was of ordinary simple glass by which the surface potentials are found to be chiefly due to the hydrogen ion concentration of the solution. In the third case a similar beaker was covered inside with a thin paraffin layer. The quartz beaker was of clear quartz and so highly insulating that it did not allow of measurements in the way described above. Relative measurements on different solutions could however be performed by successively changing one solution into the other without ever emptying the vessel more than half and without disconnecting the solution in the vessel from the calomel electrode. Such measurements agreed to within 0.01 volt.

The potential difference at the wall of the vessel is therefor far from constant, still less is it zero. Instead it is a very obvious function of the nature and concentration of the electrolyte. The writer will not enter upon a further discussion of these functions, but will refer to my other papers. Here I will only give some new measurements on the influence of concentration on metallic electrodes. The measurements will clear up a very deceptive phenomenon, which is observed by the electrostatic methods and which have led Ewell as well as (earlier) the present writer to erroneous ideas on the effect of concentration.

For the potentials of a Vienna normal glass beaker, filled with copper sulphate solutions, connected with a copper electrode, I got the values of Table I.

TABLE I.

Vienna normal glass—solution of $CuSO_4$–Cu^+

Conc. of $CuSO_4$.	Potential (—an Arbitrary Constant).
1 normal	+ 18 millivolt
0.1 "	+ 41 "
0.01 "	+ 79 "

Apparently the copper electrode gets more positive, when the concentration is decreased, though the theory of Nernst would predict the contrary. The absolute values of the variations, however, are of the same order of magnitude as in this theory.

[1] Zeits. f. Phys. Chemie, 63, 326, 1908.

These phenomena, however, are easily shown to be a consequence of glass boundary potentials by connecting the solutions with a calomel normal electrode. I thus got the readings of Table II.

TABLE II.

⁻Vienna normal glass—solution of $CuSO_4$–n1KCl–HgCl–Hg⁺

Conc. of $CuSO_4$.	Potential (—an Arbitrary Constant).
1 normal	± 0 millivolt
0.1 "	+ 39 "
0.01 "	+ 94 "

The liquid potentials here are rather small, thus the boundary potential obtained from this kind of glass (unlike that obtained from common simple glass sorts) is found to give considerable variations by altering the concentration of the neutral salt.

As the arbitrary constant is the same in Tables I. and II. we get the values of the E.M.F. of the circuit in Table III. which agree well enough with direct measurements by Labendrinski.[1]

TABLE III.

⁻Hg–HgCl–n1KCl–solution of $CuSO_4$–Cu⁺

Conc. of $CuSO_4$.	E.M.F. (Borelius).	E.M.F. (Labendrinski).
1 normal	+ 18 millivolt	+ 20 millivolt
0.1 "	+ 3 "	− 1 "
0.01 "	− 15 "	− 21 "

As a summary of his investigation the writer contends that the electrostatic measurements on electrode potentials have given no proof against the usual theory of their absolute values. Using common values for the electrode potentials we get from Ewell's electrostatic measurements an E.M.F. for a combination

⁻electrolyte—glass—metal film⁺ = about + 0.5 volt

only if such a value can be shown to be inacceptable, can an attack be made, from electrostatic measurements, against the zero point of the drop electrode.

PHYSICAL LABORATORY OF UNIVERSITY,
LUND, SWEDEN,
February, 1916.

[1] Zeit. J. Elektrochemie, 10, 77, 1904.

A STUDY OF THE LAW OF RESPONSE OF THE SILICON DETECTOR.

BY LOUISE S. MCDOWELL AND FRANCES G. WICK.

THE special form of silicon detector receiver designed by E. Merritt for use with short electric waves and reported upon at the meeting of the Physical Society, February 27, 1915, showed certain peculiarities which made desirable a further study of the device. The investigation described in the following paper includes, first, a study of the receiving device and the conditions under which it can be used to best advantage, and secondly a study of the law of response of the silicon detector with a

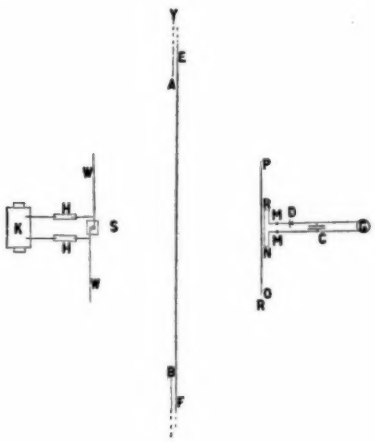


Fig. 1.

variation in the energy of the incident wave produced by the rotation of a screen of parallel wires.

The oscillator, receiver, and screen were arranged as shown in Fig. 1. The oscillator, *S*, consisted of a small spark gap in kerosene, extended by two straight aluminum wires, *WW*, to a length of 51 centimeters, and connected through water resistances, *HH*, to the secondary of a small automobile induction coil, *K*, using about six volts. The water resistances introduced served to damp any oscillations from the coil which might have produced disturbances. When carefully adjusted this arrangement

produced a spark which fluctuated so slightly that sets of observations made at intervals of half an hour or more checked almost exactly.

The receiver consisted of a silicon detector, *D*, in series with a paper telephone condenser, *C*, of one microfarad capacity, and with a loop of wire, *NR*. The connections to this loop were made by mercury cups, *MM*, to allow convenient changing of both the shape and size of the loop. A sensitive galvanometer, *G*, Leeds and Northrup Type H, was shunted around the condenser. To avoid reflections the galvanometer was placed at a distance of two and one half meters behind the receiver. An aluminum rod, *OP*, acting as a resonator, was supported parallel to the outer wire of the loop and very close to it. The greatest sensitiveness was obtained when the two wires were practically in contact. The length of the resonator was 44.5 centimeters, the length which was found to give the maximum response to the wave-length used, about 100 centimeters.

Between the receiver and the oscillator and parallel to them was placed a screen, *EF*, supported in such a way that it could be rotated through known angles. It consisted of iron wires stretched parallel to each other about three centimeters apart, upon a wooden frame two meters square. The ends of the wires were fastened to screw eyes so that they could be tightened when necessary. In all but the preliminary experiments there was an additional fixed screen of tin and wire netting, *XY*, three meters high and four meters broad, completely dividing the room except for an opening, *AB*, left in the center. The rotating screen was placed close to this opening, on the side toward the receiver, at distances varying from five to ten centimeters for different sets of observations. The opening in the fixed screen was at first square, 110 centimeters on an edge, later circular, with a diameter of 125 centimeters. The distance of the oscillator from the fixed screen varied between 120 and 200 centimeters. The distance of the receiver from the fixed screen was about 230 centimeters.

Merritt, in his experiments with the receiving device, had noted that when the screen was placed with its wires parallel to the oscillator, the position which should allow no transmission, the galvanometer deflection indicated that there was still considerable effect upon the receiver, amounting, at the least, to about one fifth of the maximum effect, when the wires were vertical, the position for complete transmission. The cause of this residual effect and the conditions under which it would be reduced to a minimum were unknown. He observed also that as the wire screen was rotated through 360° there was a variation in the response in the different quadrants. Early in the present experimental work it was found that when the resonator, *OP*, Fig. 1, was removed, the

receiving apparatus still responded, although weakly, to waves from the oscillator. The receiver was then studied with two ends in view: first to discover what changes in the design would affect the response without the resonator, *i. e.*, to what extent it depended upon the shape and size of the loop and the plane of the receiver, and how it could be reduced to the minimum consistent with sensitiveness of the receiver as a whole; second, with the receiver thus made as free as possible from defects of construction, to discover the cause of the residual effect when the screen was in the position of no transmission. Experiments were made with the plane of the receiver both vertical and horizontal.

RECEIVER IN THE VERTICAL PLANE.

The receiver was mounted on a T-shaped board and suspended by rubber bands from a crossbar rigidly fastened to the ceiling. To prevent reflections, all removable metal was taken from the room and from the adjoining rooms. There remained, however, iron shelf brackets and two overhead steam pipes running at right angles to the oscillator. To reduce any difficulties arising from reflections from the metal, the room was completely divided crosswise by the fixed screen described above, and the rotating screen was placed in front of the opening. The residual effect was found to be considerably reduced by the introduction of the screen.

With these precautions the screen was rotated through 360° and readings were taken every 20° both with and without the resonator. From the observations made three curves were plotted, in which the ordinates were galvanometer deflections and the abscissae the angles between the parallel wires of the rotating screen and the vertical. The first curve

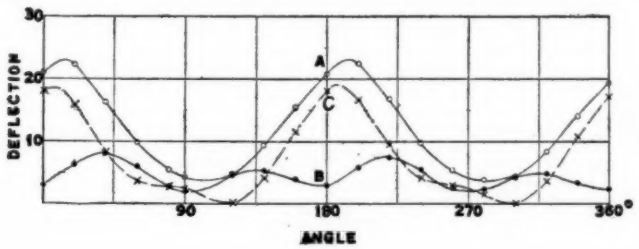


Fig. 2.

Response of the receiver in a vertical plane. *A*, resonator curve. *B*, non-resonator curve. *C*, difference between *A* and *B*.

was obtained with the resonator, the second without the resonator, and the third showed the difference between the two. Curves so obtained are shown in Fig. 2.

The resonator curve, *A*, has a maximum at 15° from the vertical position and a minimum at 100°. Curve *B*, obtained without the resonator, showed four maxima at approximately the 45° positions, such as would occur if the vertical component of the wave transmitted affected the vertical wires of the receiver. Curve *C*, the difference curve, was thought to represent more nearly than curve *A* the effect upon the resonator alone, although the lack of symmetry suggests a mutual action between the resonator and the loop. In order to detect to what extent the lack of symmetry in the curves was due to reflections of waves by material inside the building, the apparatus was moved outdoors and a similar set of observations was made. These outdoor curves were similar in form to those taken indoors and therefore the apparatus was replaced in the room where the disturbing factors remained more nearly constant.

To determine the effect of the design of the receiver upon the response without the resonator, series of observations were made with loops of various shapes and sizes. To get the effect upon the loop alone the receiver was screened by a tin cylinder up to the mercury cups, *MM*, Fig. 1. To test the response to the vertical and horizontal components of the transmitted waves, loops were made with the lengths of the vertical

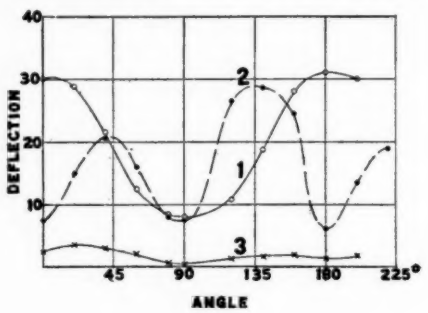


Fig. 3.

Curves showing effect of change in size and shape of loop. 1, horizontal loop equal in length to resonator. 2, vertical loop equal in length to resonator. 3, short horizontal loop.

and horizontal portions of the wire in varying ratios. Curves showing extreme variations are given in Fig. 3.

Curve 1 was obtained with a loop having its length in the horizontal direction equal to that of the resonator and its height one centimeter. It shows maxima at 0° and 180°. The addition of the resonator produced no effect. Curve 2 was produced by a loop of the same dimensions as Curve 1 but with the longer dimension vertical. The maxima occur at approximately 45° and 135° as was to be expected. Curve 3 was obtained with a loop about 13.8 centimeters long and .8 centimeter high. The

maxima occur at 20° and 160°. Owing to the entire lack of resonance the response was weak. The conclusion to be drawn from these curves is that the horizontal portions of the loop give a maximum response at 0° and 180°, the vertical portions at 45° and 135°. In any form of loop used in a vertical plane there will be both horizontal and vertical parts. The receiver will therefore respond both to the horizontal and vertical components of the waves received, and the position of the maxima will vary with the particular form.

Receiver in the Horizontal Plane.

Since for the study of the law of the detector it was desirable to eliminate as far as possible all response to the vertical component, the entire receiver was placed in the horizontal plane and suspended as before by rubber bands. To reduce still further the response without the resonator the short loop which had given the minimum effect was used. The screen was rotated through 360° and readings were taken every 20° with and without the resonator as before. The curves obtained showed the effect without the resonator to be a much smaller fraction of the entire response than under the best conditions with the receiver vertical, since only those wires in the detector circuit which were parallel to the resonator were in a position to respond to the incident wave. As a further precaution oscillator, receiver, and rotating screen were carefully centered. Curves obtained under these conditions both with and without the resonator had their maxima at 0° and 180° and their minima at 90° and 270°, and the effect without the resonator was extremely small.

The effect for the 90° position of the rotating screen, the position of no transmission, was still to be considered. This residual effect with the resonator was about 15 per cent. of the maximum and indicated that with the screens used there were diffraction effects which, as might be expected, were more noticeable with the resonator than without. In order to investigate the diffraction the receiver was placed in a tin box. The response to the waves did not entirely cease until the tin cover was made completely to enclose the receiver; even a small opening in the cover produced a decided deflection of the galvanometer. That the effect was due to the action of diffracted waves on the receiver was further shown by the fact that with the rotating screen in the position to allow no transmission a wire reflector back of the receiver at varying distances clearly indicated the presence of nodes and loops at distances apart which showed the wave-length to be that of the original wave. Since the exact determination of the wave-length was not essential to the present problem the nodes and loops were located here as in the earlier determination of

the wave-length simply by moving the small reflecting screen back and forth until the galvanometer reading was a minimum, then slowly changing the position until the reading was a maximum. In this way the nodes and loops were located for a distance of about two wave-lengths. The average distance from node to node was found to be slightly more than fifty centimeters making the wave-length approximately one hundred centimeters. A similar effect was obtained by motion of the reflecting screen in various parts of the room. Motion of an observer produced an effect of such magnitude that it was found necessary to maintain fixed positions when any observations were in progress. An observer in position to cut off the diffracted waves from one edge of the screen produced a marked change in the deflection. Since the fixed screen was not square the effect due to the interference between waves coming from the sides and those over the top and bottom of the screen might be expected to vary with the position of the oscillator and receiver. Graphical determinations based on the dimensions of the apparatus and the length of the wave used were made to find the positions for the oscillator and receiver in which diffraction effects were least. Observations verified these determinations for positions of greatest and least response, but the difference due to change in position was found to be so small as to be negligible

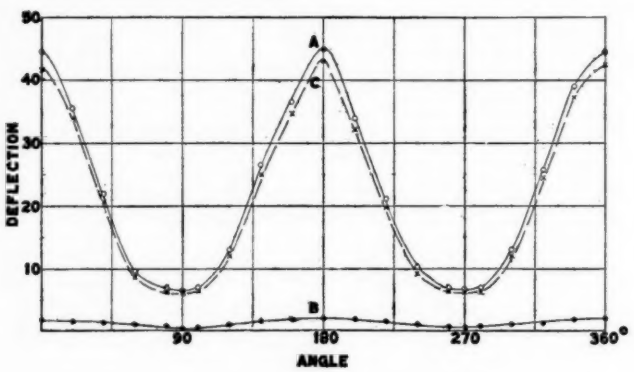


Fig. 4.

Response of the receiver in a horizontal plane. *A*, resonator curve. *B*, non-resonator curve. *C*, difference between *A* and *B*.

in comparison with the entire diffraction effect. The magnitude of these diffraction effects is not surprising considering that the length of the wave used was comparable with that of ordinary sound waves and the dimensions of the opening in the screen were but slightly greater than a wave-length. Since diffraction effects were so large the possibility that the varying distance from the corners of the square opening

to the edge of the rotating screen might alter the diffraction effects for different positions was considered. The square opening originally used was therefore replaced by a circular one, but no difference in the results was observable.

Final observations were made with the receiver in the horizontal position at a distance of 225 centimeters from the fixed screen and with the oscillator at distances from the screen ranging from 120 to 230 centimeters. A typical set of curves is shown in Fig. 4. It will be noted that the maxima and minima of the curves with and without the resonator are at the same points, that the effect upon the receiver without the resonator is very small, and that Curves *A* and *C* are therefore almost identical.

THE LAW OF THE SILICON DETECTOR.

Since for the final curves obtained the receiver was so adjusted as to respond only to the horizontal component of the transmitted wave it seemed possible to use the data to determine the law of response of the silicon detector with a variation in the intensity of the incident wave. The data already obtained showed the response of the receiver for each position of the rotating screen. Since only the component of the wave at right angles to the wires of the screen could be transmitted the amplitude of the transmitted wave varied as the cosine of the angle between the wires and the vertical. As the receiver was capable of responding only to horizontal waves the transmitted component suffered a second resolution at the receiver, which again cut down its amplitude by the cosine of the same angle. Hence the amplitude of the component of the wave to which the receiver responded was proportional to the square of the cosine of the angle between the vertical and the wires of the screen. Presumably the amplitude of the oscillations set up in the receiver for different positions of the screen was proportional to the amplitude of this received component and hence to the square of the same angle. The rectified current through the detector should therefore be proportional to some power of the cosine of this angle.

In determining the law only those data were considered in which the values of the current obtained without the resonator were small. The corrected values of the galvanometer deflections, *i. e.*, the differences between the deflections with and without the resonator, were used as representing more nearly the response to the received wave of the resonator alone. With the galvanometer used the deflections were proportional to the current. For each set of readings two curves were plotted, with the galvanometer deflections as abscissæ and in one case the second, in the other

the fourth powers of the cosines of the angles as ordinates. In all nine sets of readings were so plotted. Of these three were rejected because the maximum was shifted four degrees to the one side or the other. One set was rejected because the detector was so insensitive that the straight line fitted the second and the fourth power values almost indifferently well, although with a slight advantage in favor of the fourth power. In the remaining five cases, in none of which was there a variation in the position of the maximum of more than two degrees from 180°, the straight line fitted the fourth power values decidedly better. Typical curves are shown in Figs. 5 and 6. Fig. 6 is for the same set of data as Fig. 4.

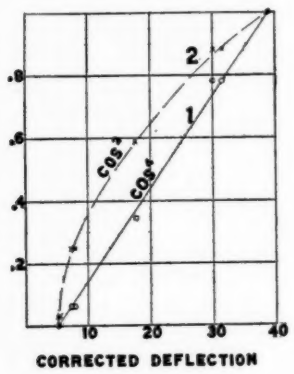


Fig. 5.

The law of response of the silicon detector.

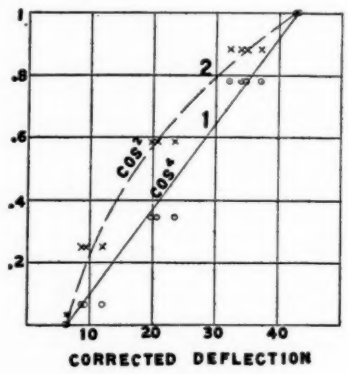


Fig. 6.

The law of response of the silicon detector.

It will be seen that there are still noticeable variations in the position of corresponding points in the four quadrants.

Since even under the best conditions there was rarely an exact coincidence of readings for corresponding points in the four quadrants these results were checked for each set of readings by noting the agreement with the straight line of the values for each of the four quadrants separately. In six instances the straight line fitted the fourth powers far better, in three instances decidedly better, and in five instances somewhat better. In only three instances were the results indeterminate and in no case did the straight line fit the second powers better.

A further study of the curves previously rejected showed that in one case the lack of symmetry was due to a progressive increase in the strength of the spark. In this case in two of the quadrants the straight line fitted the fourth powers decidedly better, in the other two quadrants it did not fit either the second or fourth power values although in one quadrant the variations of the fourth power values were the greater. In the second case the cause of the lack of symmetry was not so evident.

Since the spark remained steady and the non-resonator curves showed no evidence of a lack of horizontalism in the loop it was probably due to a slight displacement from the horizontal of the resonator itself. The results in this instance were entirely inconclusive. In the third case the spark was unsteady and the loop not entirely horizontal as shown by two decided humps in the non-resonator curve, yet even here in the two quadrants in which the non-resonator values were small the straight line fitted the fourth power values closely. In the light of these results it seems safe to conclude that the rectified current is proportional to the fourth power of the cosine of the angle between the vertical and the wires of the rotating screen.

Since the amplitude of the oscillations in the receiver is presumably proportional to the square of the cosine this result indicates that the rectified current through the silicon detector is proportional to the square of the oscillating current in the receiver. Austin[1] in his study of the silicon detector reached the conclusion that for alternating currents of ordinary frequencies and for oscillating currents of a frequency of 140,000 the rectified currents are approximately proportional to the square of the alternating currents. The results of the investigation of the writers confirm this law for a frequency of approximately 3×10^8.

In conclusion the authors wish to acknowledge their indebtedness to Professor Ernest Merritt for frequent suggestions during the progress of the work and to thank the department of physics of Cornell University for permission to work in the Rockefeller Laboratory during the summer of 1915.

Wellesley College,
Vassar College.

[1] Bull. Bur. Stand., 5, 133, 1908.

SOME PROPERTIES OF MERCURY DROPLETS IMPORTANT IN ELECTRONIC CHARGE MEASUREMENTS.

BY L. W. MCKEEHAN.

INTRODUCTION.

THE work described below was incidental to additional investigation of the correction to Stokes's formula in gases,[1] using mercury spheres. Mercury has the advantage of being easily obtained in the form of small drops by several different methods; it is a liquid and therefore sphericity is assured;[2] its density and viscosity are known and are nearly constant at room temperature. In earlier work mercury spheres had been abandoned on account of the high reflecting power of their surfaces and the consequent difficulty experienced in obtaining a definite image under a microscope when the radius is only a few wave-lengths of light.[3] The method finally devised, and described below, removes this difficulty completely, and permits measurement of the radius of such spheres with a probable error of one or two per cent., and without systematic errors of comparable amount. The homogenity of such mercury droplets, and the constancy of their mass, form, and density have been matters of dispute,[4] so it seemed proper to investigate these properties, if possible, with the aid of the measuring device already constructed. The experiments show that constancy of mass is incompatible with the continued purity of the material in a gas, and that hitherto neglected chemical properties of the metal profoundly modify its behavior in this state of subdivision without correspondingly important changes in the appearance of the drops.

EXPERIMENTS.

Small spheres in a wide range of suitable sizes were deposited on a steel spring from the mercury vapor carried by a light puff of dry air sent across the surface of freshly distilled and nearly boiling mercury. The

[1] L. W. McKeehan, PHYS. REV. (1), 32, 341, March, 1911.

[2] J. Perrin suggests however, that vibrations of the surface may be caused by unbalanced molecular impacts. C. R., 152, 1165, May, 1911.

[3] J. Zeleny and L. W. McKeehan, PHYS. REV. (1), 30, 535, May, 1910.

[4] A. Schidlof and A. Karpowicz, C. R., 158, 1992, June, 1914; Ph. ZS., 16, 42, Feb., 1915; F. Ehrenhaft, Ph. ZS., 16, 227, June, 1915; 228, Aug., 1915; A. Schidlof, Ph. ZS., 16, 372, Oct., 1915.

spring was snapped against the surface of a glass plate rotating under a measuring microscope; and this plate could be enclosed if desired during the remainder of an experiment.

A microscope plate micrometer,[1] was used in measuring the spheres, one centimeter on its scale corresponding to about 7.5×10^{-6} cm. on the object measured. The accuracy of a single setting on a fixed mark is approximately 3×10^{-6} cm. Incandescent lamps with frosted globes were placed on each side of the microscope in the lower focal plane; *i. e.*, in a horizontal plane through the drop, and about 20 cm. from the axis of the microscope. When a sphere is brought to the center of the field by rotating the glass plate, the two reflected images of these lamps formed by the spherical mercury mirror appear as point source diffraction patterns against the dark background of the sphere itself. When the central disc of each pattern is as well-defined as possible, and the outer fringes are correspondingly inconspicuous, the distance between centers is measured, the width of the platinum cross-hair (0.0006 cm.) being so chosen that it can be seen clearly against the bright disc. Experiment shows that a variation in focus sufficient to make the central disc insignificant in luminosity in comparison with the first diffraction band (a variation that could not remain unnoticed in practice) does not affect the distance between the centers of the patterns whereas the same variation in focus blurs the apparent outline of the sphere enough to render impossible any measurement of its diameter by the usual method. The lateral illumination is varied by iris diaphragms or condensing lenses, or by moving the lamps along guides provided for that purpose, to give patterns of suitable brightness with spheres of different sizes. A diffuse illumination of the background makes the work less fatiguing to the eye without increasing the difficulty of making settings. A measurement, in the following paragraphs, means the average of ten consecutively measured diameters (twenty settings of the cross-hair) taken alternately in opposite directions to eliminate temperature drift across the field. This was otherwise reduced to a negligible amount by leaving all lights burning continuously for several days, the temperature attained being about 26° C. The large number of settings chosen minimizes the effect of accidental displacements due to jarring of the apparatus during a measurement. These sometimes occur, since the glass disc is turned magnetically and held at any position merely by the slight friction of its pivot, but the whole apparatus is much more rigidly constructed than that previously used, and disturbances due to tremors of the supporting pier, formerly so troublesome, are no longer observed.

[1] J. Zeleny and L. W. McKeehan, PHYS. REV. (1), 32, 530, May, 1911.

The measurement above described gives the quantity $a_1\sqrt{2}$, where a_1 is the radius of the spherical mirror. Calculation shows that the deviation from sphericity is negligible.[1] A correction is, however, necessary if we wish to know the radius, a, of the sphere before it settled upon the glass plate, since the sphere of radius a_1 lacks a segment whose volume depends upon the angle of contact, α, between mercury and glass. This need only be known approximately to give a quite accurately, and the surface force is so great in comparison with the gravitational force that we may assume this angle constant even when the truncated sphere changes volume rapidly. If $\alpha = 148°$, $a = 0.93\ a_1$, and would be still smaller if α were less.[2] Since contamination of surface reduces α, the rates of decrease in radius observed below are, if anything, too small.

Measurements have been repeated at intervals on about fifty spheres, made in fifteen lots, the time of making and of each measurement being recorded. The same sphere was under observation for as long as ten days. Continuous diminution in size occurred in every case, but the rate of decrease in radius $(-da/dt)$ may be very different for different spheres of the same age and radius. Each sphere shows a variation in the rate of decrease that depends upon the age and the previous history of the sphere.

Spheres exposed to either dry or moist air for from one to forty-eight hours reach a final stage in which the rate of decrease in radius is to first approximations independent of time and inversely as the radius, between $a = 10^{-4}$ cm., and $a = 10^{-3}$ cm. The value of $-da/dt$ for $a = 4 \times 10^{-4}$ cm. is about 1.4×10^{-10} cm./sec.[3]

The initial value of $-da/dt$ may be only a little greater than the value in the final stage, or many times greater (as high as 1.5×10^{-3} cm./sec. in one case). In the former case the final stage is reached in a short time, in the latter case the time required to reach the final stage is the longer the greater the value of a. The initial rate appears not to depend upon a, but the larger spheres are more uniform in their behavior than the smaller ones. The total decrease in a before the final stage is reached varies from 10 to 50 per cent., the *maximum* per cent. of decrease being greater for the smaller spheres. The variation of a with the time is shown for typical spheres in Fig. 1.

Spheres surrounded by an atmosphere of illuminating gas (carbon

[1] F. Bashforth and J. C. Adams, Capillary Action, Camb. Univ. Press, 1883.

[2] O. W. Silvey does not mention such a correction. Its value in his experiments would be difficult to estimate since the spheres were supported for measurement on oiled steel needles. PHYS. REV. (2), 7, 87 and 106, Jan., 1916.

[3] A similar law for the evaporation of iodine spherules was found by H. W. Morse, Amer. Acad. Proc., 45, 363, April, 1910.

monoxide and hydrogen) immediately after being formed in air showed the same initial peculiarities and about the same range in the initial values of $-da/dt$ as spheres left in air, but the later stages are entirely

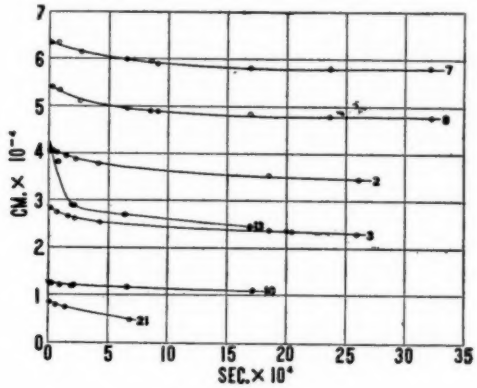


Fig. 1.

Spheres in air. Curves 2, 3, 7, 8, 21, are typical. Curve 10 shows a low initial rate of decrease. Curve 13 shows a high initial rate of decrease.

different, as shown in Fig. 2. If the initial rate is high it changes very little with time until the radius is less than 5×10^{-5} cm. Beyond this point the measurements cannot be carried with the intensity of illumination so far employed, but the rate must finally decrease, for the particle remains visible longer than it would if the initial rate were maintained to the end. If air is admitted during the period of rapid decrease the subsequent behavior is like that of a new sphere. If the initial rate of decrease is low it rises to a value of the same order as the initial rate for the class last mentioned, remains constant at this high value for a time, and finally sinks again to a low value. The last effect may or may not occur before the sphere is too small to measure, and is easiest to

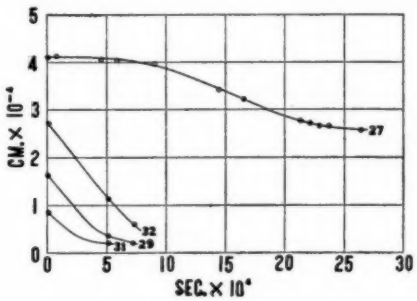


Fig. 2.

Spheres in illuminating gas. Curves 29, 31, 32, are typical. Curve 27 shows a low initial rate of decrease.

detect in the case of spheres originally of large size. If resolution of the image is still possible when it occurs the surface is seen to be roughened, the appearance being similar to that of an orange peel, and the reflecting power is greatly reduced.

Effects similar to those last described are also observed when spheres that have reached the final stage in air are then kept in illuminating gas for a further period of time. If such spheres are treated with a drop of

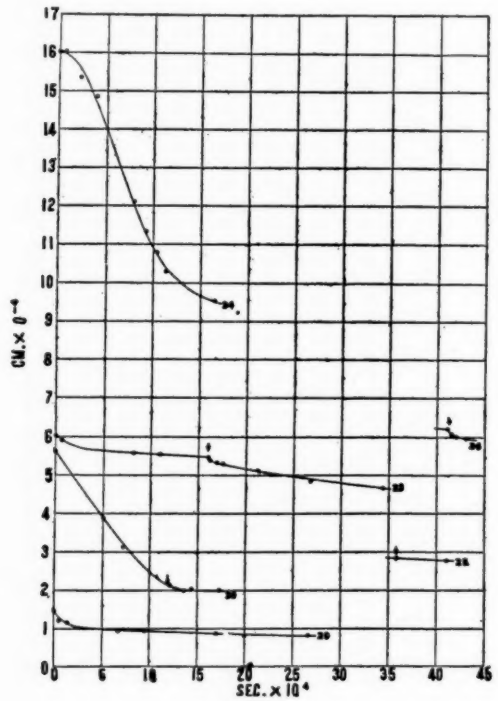


Fig. 3.

Miscellaneous effects. Curve 20 is typical for a sphere kept in air. Curve 23 shows effect of washing with alcohol at time marked with arrow, sphere kept in air. Curve 25 shows effect (negligible) of washing with water at time marked with arrow, sphere kept in air. Curve 26 shows effect of washing with water at time marked with arrow, sphere kept in air. Curve 30 shows effect of replacing illuminating gas by air at time marked with arrow. Curve 34 shows effect of replacing air by illuminating gas at time zero (sphere was an old one).

water or alcohol (the volume of such a drop will be at least 10^{12} times that of the mercury) which is then allowed to evaporate, the rate of decrease is either unaffected or it is increased. If the latter is the case the subsequent behavior in air is like that of a new sphere. Fig. 3 shows examples of these effects.

The rate is little, if at all, affected by a moderate velocity of circulation

of the surrounding air or other gas, or by illuminating the sphere only occasionally instead of continuously.

Spheres made and measured in illuminating gas showed a high rate of decrease but finally became dirty and distorted. Similar experiments in carbon dioxide show the latter effect occurring sooner.

By condensing a great number of spheres directly upon the glass plate it was found possible to supersaturate an atmosphere of carbon dioxide with mercury vapor to such an extent that the larger spheres grew slowly while the smaller spheres decreased. In a particular experiment the radius of spheres in (unstable) equilibrium with the vapor was 1.1×10^{-4} cm.

DISCUSSION OF RESULTS.

The rate of evaporation from a clean mercury surface at the average temperature of experiment is more than sufficient to account for the maximum rate of decrease observed.[1] Since circulation of the gas was found to have little effect upon the rate it may be assumed that diffusion of the vapor is able to keep its partial pressure in the neighborhood of an isolated sphere of the size used very far below the saturation pressure.

This is additionally probable because the curvature of the surface of such a sphere is so great that it would evaporate readily even in an atmosphere saturated with respect to a plane surface. The presence of even a thin layer of gas not sharing the general circulation would explain the low maximum rate of evaporation here noted (less than one per cent. of the theoretical maximum in a perfect vacuum). Since Knudsen[2] found that the maximum rate persisted for less than four seconds even in the best vacuum it seems reasonable, however, to attribute the discrepancy mainly to contamination of the surface, especially since the still lower rates obtained are evidently due to this cause. On account of the protection afforded by the glass plate the rates of decrease observed are no doubt somewhat smaller than they would be for freely falling spheres of the same mass (of actual radius a).

The contamination that occurs in air is inferred to be a thin but coherent and translucent layer of mercuric oxide,[3] which may be removed mechanically by a liquid or chemically by a reducing atmosphere such as illuminating gas.[4] The latter also naturally prevents the formation of the oxide on a clean sphere. Even if the removal is incomplete the coherence of the oxide layer is destroyed and fresh surface is exposed.

[1] M. Knudsen, Ann. d. Phys., 47, 697, Aug., 1915.

[2] Loc. cit.

[3] G. B. Taylor and G. A. Hulett predict the formation of this oxide at room temperatures. Journ. Phys. Chem., 17, 565, Oct., 1913.

[4] L. Moser and O. Schmid, ZS. Anal. Chem., 53, 217, 1914.

The appearance of dirt on the surface at a later stage suggests that the formation of a carbonate accompanies the reduction. The oxide layer formed on the smaller spheres is apparently more porous than that formed on the larger ones. This may be due to the greater fractional decrease in area and consequent more frequent disturbance of the layer for the same rate of decrease in radius in the former case. Spectroscopic examination of the reflected light is suggested as an independent method of investigating these points.

The experiments of A. Schidlof and A. Karpowicz[1] agree very well with the explanation offered above, the persistence of evaporation in nitrogen but not in air being particularly striking. The experiments of F. Ehrenhaft[2] show no less strikingly the effect of the oxide layer that was certainly formed under his experimental conditions.

The alterations in surface observed would have an effect upon the correction to Stokes's formula that might well be different in the case of different drops as prepared by condensation from vapor. This variation would make electronic charge determinations especially erratic for very small spheres, where the correction to Stokes's formula is large. Atomization should prove a more reliable method for obtaining initial uniformity, but it seems clear that sufficient purity of surface is a good deal harder to get and to keep than has hitherto been realized.

PHYSICAL LABORATORY,
UNIVERSITY OF MINNESOTA.
April 14, 1916.

[1] Loc. cit.
[2] Loc. cit.

THE EVAPORATION, CONDENSATION AND REFLECTION OF MOLECULES AND THE MECHANISM OF ADSORPTION.

By Irving Langmuir.

PART I.

IN a recent paper R. W. Wood[1] describes some remarkable experiments in which a stream of mercury atoms is caused to impinge upon a plate of glass held at a definite temperature. With the plate at liquid air temperature all the mercury atoms are condensed on the plate, whereas with the plate at room temperature all the atoms appear to be diffusely reflected. Wood seems to consider that this is a real case of reflection.

There is, however, another way of interpreting the experiments, which, I think, is more in harmony with other facts than that suggested by Wood.

We may, for example, consider that all the atoms of mercury which strike the plate *condense no matter what the temperature of the plate.* When the plate is at the higher temperatures the condensed atoms may reëvaporate again so rapidly that the surface remains practically free from mercury. At first sight it might appear that there is no essential difference between this reëvaporation and a true reflection, but more careful consideration shows that the two phenomena are quite distinct. The difference would be manifest if the so-called reflection were studied at intermediate temperatures. In the case of reflection the number of atoms reflected would always be proportional to the number striking the surface, whereas, according to the reëvaporation theory, the number leaving the surface can never exceed the normal rate at which mercury evaporates into a perfect vacuum.

Wood states that he intends to undertake experiments at intermediate temperatures, and in view of this I should be loath to take up a discussion of the matter at present if it were not for the fact that much of my work during the last few years has had a very direct bearing on the question of the condensation versus the reflection of gas molecules.[2]

[1] Phil. Mag., *30*, 300, 1915.

[2] In this connection, for the sake of historical accuracy, attention may be called to the fact that the rectilinear propagation of molecules in vacuo, which Wood and Dunoyer (Comptes Rendus, *152*, 593, 1911) have described, has long been familiar to incandescent lamp manufacturers not only in the case of tungsten lamps, but also with carbon lamps. Professor

As a result of this work, which I shall briefly describe in the following pages, I have gradually become convinced that molecules and atoms of all kinds show little or no tendency to be reflected from a solid surface against which they strike. In the case of metal vapors condensing on the corresponding metals, the evidence seems to indicate that not over one atom per thousand is reflected, if indeed, there is any reflection whatever. However, with molecules of the so-called permanent gases striking surfaces covered with adsorbed films of gas molecules, there is some evidence that a certain amount of reflection may occur. When hydrogen molecules strike a hydrogen covered surface at high temperatures it is possible that as many as 81 per cent. of the molecules are reflected. There is reason to believe that this represents the maximum possible degree of reflection and that with gases other than hydrogen and helium, the amount of reflection is always less than 50 per cent., no matter what may be the nature of the solid surface.

I. EXPERIMENTAL DATA.

Evaporation and Condensation.—In connection with an experimental determination of the rate of evaporation of tungsten filaments in a high vacuum[1] the following relation between the vapor pressure p and the rate of evaporation m (in grams per sq. cm. per second) was derived from the principles of the kinetic theory

$$m = (1 - r)\sqrt{\frac{M}{2\pi RT}}\,p. \tag{1}$$

Here M is the molecular weight of the vapor, R is the gas constant, and

W. A. Anthony, in a paper read before the American Institute of Electrical Engineers at New York in 1894, described this phenomena as follows (Trans. Amer. Inst. Elect. Eng., *11*, 142, 1894): "In the old Edison lamps the filament was copper-plated to the platinum wires. When a break in the filament occurred near the junction, the arc vaporized the copper and covered the bulb with a coating of metallic copper, except that a line of clean glass was often left on the side opposite the break, the line being the shadow of the unbroken leg of the filament. . . . The plain old-fashioned unpretentious vapor tension that bursts our steam boilers is all-sufficient to account for this rectilinear projection across the lamp bulb when there is nothing in the way." In the very active discussion which followed, Professor Elihu Thomson said "I am confident that I have seen it (this phenomenon) in series lamps when the carbon broke. In a good vacuum the carbon vapor condensing would give rise to particles which would move in rectilinear paths. The shadow effect is dependent on a *local* evolution of vapor, with a part of the wire or filament between the point of evolution and the opposite glass surface. I am also confident that I have seen platinum shadows." In the further discussion, J. W. Howell said, "The molecules of carbon set free by evaporation, fly from the filament as Professor Anthony says, in straight lines. They are projected from every part of the filament and . . . cast shadows on the globes. The reason why they do not cast shadows in most lamps is that the filament is not all in one plane." Mr. Howell then exhibited to those present, both carbon and platinum lamps which showed distinct shadows.

[1] Langmuir, PHYS. REV. *2*, 329, 1913, and Phys. Zeitsch., *14*, 1273, 1913.

r is the coefficient of reflection of the vapor molecules which strike the surface of the solid (or liquid). It was stated at that time (1913) that "There are good reasons for believing that the reflection of vapor molecules from the surface takes place to a negligible degree only," and there followed a discussion of Knudsen's results on the heat conductivity of gases at low pressures which we shall consider in more detail below.

The above formula, taking $r = 0$, was then used to calculate the vapor pressure of tungsten from the experimental data on the rate of evaporation.

Subsequently[1] the vapor pressures of platinum and molybdenum were determined by the same method. At that time the question of the possible reflectivity was discussed as follows: "That the atoms of metal which evaporate from a hot wire are not reflected to any perceptible extent upon striking a surface, has been shown by many experiments in this laboratory. For example, if a single loop tungsten filament be heated in a highly exhausted bulb to such a temperature that the evaporation is fairly rapid, a dense black coating of the metal will be deposited uniformly on the glass. If, however, a screen, say of mica, be placed near the filament, that part of the bulb in the 'shadow' of the obstruction will be perfectly clear with sharp boundaries. This shows that the atoms of tungsten travel in straight lines from the incandescent wire to the bulb, and that, at least from cold tungsten surfaces, the reflection of the tungsten atoms is negligible." The other evidence referred to here will be briefly described in connection with the discussion of chemical phenomena and thermionic emission.

Experiments have been made to determine the vapor pressures of silver, gold, iron, copper and nickel by this method, and the results will soon be published. The experiments with silver are of especial interest, since the vapor pressure of this metal has been determined by von Wartenburg by another method, so that the results have served as a test of the correctness of the theory.

The fact that the reflectivity of mercury atoms from a mercury surface at 100° C. cannot be very high follows from some work carried out by Hertz in 1882.[2] Hertz pointed out from theoretical considerations similar to those used above, that the rate of evaporation of mercury at 100° into a perfect vacuum could not exceed 0.016 gram per sq. cm. per second. Experimentally he found that a rate of evaporation as high as .0018 gram per sq. cm. per sec. could be realized. He considered that this result was merely a lower limit and that the true rate of evaporation

[1] Langmuir and Mackay, PHYS. REV., *4*, 377, 1914.

[2] Ann. Phys., *17*, 177, 1882.

must lie between the two limits given. If we calculate the maximum possible rate of evaporation of mercury at 100° C. from equation (1), placing $r = 0$ and $p = 368$ bars, we obtain $m = .0117$, which is not very far from Hertz's calculated value of .016.

From Hertz's experimental result, together with the value calculated from (1), we may conclude that at least 15 per cent. of all the mercury atoms striking the surface must condense. By closer examination of Hertz's experimental conditions it is readily seen that his result must be much too low and the probability thus becomes strong that the amount of real reflection is very small.

Very recently, however, Knudsen[1] has accurately determined the rate of evaporation of mercury in a high vacuum, and by comparing this with the vapor pressure, using an equation similar to (1), he has been able to prove conclusively that, with a clean mercury surface, r does not exceed one per cent. That is, he finds that all the mercury atoms striking a mercury surface are condensed when the surface is at room temperature.

This result of Knudsen's, together with Wood's conclusion that reflection is absent when the glass plate is at the temperature of liquid air, indicates that there is little or no reflectivity of mercury atoms from either a solid or liquid surface of mercury.

Experiments on the formation of "shadows" in the evaporation of filaments in a high vacuum have proved that at least for surfaces at room temperature the same conclusion may be drawn regarding the reflectivity of atoms of tungsten, platinum, copper, gold, silver, molybdenum, carbon, iron, nickel and thorium.

In the case of thorium we have evidence that not even one atom of thorium out of millions is reflected when these strike a surface of tungsten at room temperature. This result was found in connection with experiments (as yet unpublished) on the effect of traces of thorium on the electron emission of tungsten. If a filament containing thorium is placed in a bulb close to a pure tungsten filament, the electron emission from the latter may be increased from 10,000 to 1,000,000 fold (according to the temperature) by heating the thoriated filaments so as to distill off a trace of thorium onto the tungsten filament. If, however, a screen be placed between the two filaments it becomes impossible (in very high vacuo) to raise the electron emission of the second filament by this means, although if any reflection of molecules from the surface of the bulb should occur it would result in the deposition of thorium on the tungsten filament.

These facts would seem sufficient to establish the following general rule.

The reflectivity of metal atoms striking surfaces of the same metals at room temperature (or lower) is zero.

[1] Ann. Phys., 47, 697, 1915.

The question remains whether the reflectivity is still zero when the surfaces are at higher temperatures and when surfaces other than that of the metal are concerned. Knudsen's work with mercury has shown that the reflectivity with this metal remains zero even at temperatures where the vapor pressure of the metal becomes fairly high.

We shall see, however, from a consideration of other cases, that the coefficient of reflectivity changes very little if at all with temperature, so that I think the above rule may safely be generalized to include metal vapors condensing on metals at any temperature.

Whether or not the same rule would apply to non-metallic substances with equal accuracy, is rather doubtful. However, we shall see from theoretical considerations that even in such cases as that of hydrogen atoms striking a surface of liquid or solid hydrogen, there is reason to believe that the amount of reflection is small.

Heat Conduction in Gases at Low Pressures.

Kundt and Warburg in 1875 predicted from the kinetic theory that there should be a discontinuity in the temperature close to the surface of a solid body which is dissipating heat by conduction into a gas at low pressure. Smoluchowski, in 1898, observed and studied this phenomenon and developed the theory of it. He found that in some gases, particularly hydrogen, the amount of heat given up to the gas by the solid was only a fraction of that which should be delivered if each molecule striking the surface reached thermal equilibrium with it before leaving.

Knudsen[1] gave the name "accommodation coefficient" to the ratio of the heat actually carried away by the gas, to that which would be carried if thermal equilibrium were reached. Knudsen measured the accommodation coefficient (α) for several gases and several different kinds of surface. The lowest value found was with hydrogen in contact with a polished platinum or glass surface, in which case Knudsen obtained $\alpha = 0.26$. With heavier gases, such as nitrogen and carbon dioxide, he found $\alpha = 0.87$.

Soddy and Berry[2] in a similar study of the heat conductivity of gases at low pressures, found that α for hydrogen in contact with platinum varied from 0.25 at $-100°$ C. to 0.15 at $+200°$. For argon they found an average value $\alpha = 0.85$, while for helium they found 0.49 at $-100°$ C. and 0.37 at $+150°$ C. The accommodation coefficients obtained with heavier gases were always close to unity.

The writer[3] has determined the accommodation coefficient of hydrogen

[1] Ann. Phys., *34*, 593, 1911.

[2] Proc. Roy. Soc., *84*, 576, 1911.

[3] Jour. Amer. Chem. Soc., *37*, 425, 1915.

in contact with tungsten at 1500° K. and obtained $\alpha = 0.19$, while nitrogen under the same conditions gave $\alpha = 0.60$.

The evidence thus far available indicates that the accommodation coefficients of the ordinary gases range from 0.19 up to unity. Only in the cases of hydrogen and helium have accommodation coefficients less than 0.8 been found at room temperature. It is interesting to note that all observers find that the coefficient for a given gas is independent of the nature of the solid, so long as it has a polished surface. This is an indication, for which other evidence will be given below, that the surfaces under the conditions of the experiments are covered with adsorbed layers of gases.

Another conclusion from the experiments is that the accommodation coefficient varies only slightly with the temperature, there being a tendency for it to decrease at higher temperatures. Thus for hydrogen the coefficient seems to decrease from about 0.35 at −190° to 0.19 at 1500° K. With both helium and nitrogen there is a slight tendency for α to decrease with rising temperature.

The probable relationship between the accommodation coefficient and the reflectivity of molecules from surfaces will be discussed below, together with other experimental data.

The "Slip" in Gases at Low Pressures.

The viscosity effect analogous to the temperature discontinuity at a surface has been called the "slip." This effect, first observed by Kundt and Warburg, has been the subject of much recent study. Knudsen[1] calculates the coefficient of slip on the assumption that the molecules striking any surface are emitted from it in directions which are absolutely independent of the original directions of incidence. By elaborate experimental investigations Knudsen obtains confirmation of his theoretical conclusions and thus justifies his assumptions. Smoluchowski[2] Timiriazeff,[3] Gaede',[4] and Baule,[5] however, conclude, on experimental and theoretical grounds, that the directions of the emitted molecules are not entirely independent of the directions of the incident molecules.

It is of interest to note that Gaede, as a result of extremely careful experimental work, concludes that the amount of specular reflectivity is negative. That is, he finds at pressures above .001 mm., and up to 20 mm., that the amount of gas which flows through a tube is *less* than that

[1] Ann. Phys., *28*, 75, 1908.
[2] Phil. Mag., *46*, 199, 1898.
[3] Ann. Phys., *40*, 971, 1913.
[4] Ann. Phys., *41*, 289, 1913.
[5] Ann. Phys., *44*, 145, 1914.

calculated by Knudsen on the assumption of completely irregular reflection. Gaede draws the conclusion that a certain fraction (sometimes as large as 50 per cent.) of the incident molecules tend to return after collision in the direction from which they came. The other observers, however, all find that the amount of gas flowing through tubes is greater than that calculated by Knudsen's formula.

Knudsen, on the other hand,[1] carried out further measurements with hydrogen at low pressures and found that there cannot be a specular reflection of hydrogen molecules amounting to more than about one per cent.

Millikan[1] has calculated the coefficient of slip from his measurements on the fall of small spheres and has concluded that the slip in air is about 10 per cent. and in hydrogen about 8 per cent. greater than would be expected, according to Knudsen's assumption regarding the absence of specular reflection.

The experimental evidence on the slip of gases at low pressures does not throw much light on the reflectivity of gas molecules, but if Millikan's interpretation of his experiments is correct they would seem to indicate that a reflectivity as high as 10 per cent. occurs in some cases.

Statistics of Chemical Reactions

(*a*) *Heterogeneous Reactions.*—The rate at which the molecules of a gas come into contact with a solid surface immersed in it, may be calculated by equation (1). Suppose a heterogeneous chemical reaction occurs at the surface of the solid body. Then, if we can measure the rate at which the reaction occurs, we may be able to calculate by Equation 1 what fraction of the collisions between the gas molecules and the solid body results in a chemical reaction. Let us call this fraction ϵ.

In order to avoid complications due to the accumulation of the products of the reaction close to the surface it will be necessary either to work with very low pressures of gases or to choose reactions which take place very slowly.

The value of ϵ may in general have any value less than unity. It is evident that the reflectivity of the gas molecules striking the surface must be less than $1 - \epsilon$ and therefore, by a determination of ϵ, we obtain an upper limit for the reflectivity.

Strutt[3] has measured ϵ for two heterogeneous reactions. In the decomposition of ozone in contact with a silver surface he found ϵ equal to unity, while in the case of the conversion of atomic nitrogen into molecular

[1] Ann. Phys., *35*, 389, 1911.

[2] Discussion before the American Phys. Soc., Chicago, Nov. 30, 1915.

[3] Proc. Roy. Soc., A, *87*, 302, 1912.

nitrogen in contact with copper oxide, he obtained $\epsilon = .002$. From this we may conclude that the reflectivity of ozone molecules from a silver surface is small. In the second case, however, it is not necessary to conclude that the reflectivity is 0.998. We shall see from the general discussion below that the small value of ϵ is probably caused by a large portion of the surface being in an inactive condition, perhaps due to its being covered with a layer of adsorbed nitrogen molecules.

In a study of the rate of attack of a heated tungsten filament by oxygen at low pressure,[1] the writer determined the values of ϵ for the reaction $2W + 3O_2 = 2WO_3$. The fraction ϵ was found to be independent of the pressure and to increase rapidly with temperature from .001 at 1270° K. to 0.15 at 2770° K.

Some recent work (as yet unpublished) has shown that at higher temperatures ϵ continues to increase so that at 3000° K. it is over 0.40. Extrapolation indicates that at still higher temperatures ϵ would reach a limiting value of about 0.7.

From these results we may conclude that the reflectivity of oxygen molecules from heated tungsten does not exceed 30 per cent. It is probable in this case also, that the small values of ϵ at low temperatures are caused by an inactive condition of the greater part of the surface, rather than by a change in the reflectivity.

Experiments on the oxidation of molybdenum filaments have led to similar conclusions in regard to the reflection of oxygen molecules.

When a wire of tungsten, or other metal capable of withstanding high temperature, is heated to 1500° K. in hydrogen at low pressure, a part of the hydrogen is converted into atomic hydrogen.[2] At very low pressures this active modification of hydrogen can diffuse long distances through glass tubing at ordinary temperatures,[3] but cannot pass even short distances through tubing cooled by liquid air.

When one considers that the pressures employed in these experiments were so low that the normal free path would be of the order of several meters, it is evident that the reflectivity of hydrogen atoms from glass surfaces cooled in liquid air must be very small, if not actually zero. With the glass at room temperature the reflectivity is probably also negligible, but the atoms then reëvaporate more rapidly and are thus able to travel considerable distances.

In connection with a quantitative study of the degree of dissociation of hydrogen at various temperatures, it has been shown[4] that *every hy-*

[1] J. Amer. Chem. Soc., *35*, 115, 1913.

[2] Langmuir, Jour. Amer. Chem. Soc., *34*, 1310, 1912.

[3] Freeman, Jour. Amer. Chem. Soc., *35*, 927, 1913.

[4] Langmuir, Jour. Amer. Chem. Soc., *37*, 457, 1915.

drogen atom striking a pure tungsten surface (at 2000–3500° K.) condenses and that 68 per cent. of all hydrogen molecules striking the surface condense.

When the tungsten filament was heated to a temperature over 2700° K. in hydrogen at a pressure below 200 bars, it was found that 68 per cent. of all the molecules striking the filament were dissociated and that this fraction remained unchanged even when the filament temperature was raised several hundred degrees higher.

The fact that this coefficient (0.68) is larger than the accommodation coefficient found for a tungsten wire at 1500° in hydrogen (0.19) requires some explanation. It seems at first sight paradoxical that 68 per cent. of the molecules reach chemical equilibrium and are dissociated, whereas at lower temperatures only 19 per cent. reach thermal equilibrium before leaving the surface. In a recent paper[1] the writer gives independent evidence that at lower temperatures the tungsten surface is practically completely covered with a layer of hydrogen molecules, whereas at higher temperatures only a minute fraction of the surface is so covered. Thus the coefficient 0.19 applies to hydrogen molecules striking a surface already covered with an adsorbed layer of hydrogen molecules, while the coefficient 0.68 applies to hydrogen molecules striking an absolutely clean tungsten surface.

Some interesting data on the reflectivity of molecules from a platinum surface have been obtained in connection with a study of the combustion of hydrogen and carbon monoxide at low pressures in contact with a heated platinum wire.[2] In these experiments a platinum filament was mounted in the center of a spherical bulb of four liters' capacity, provided with an appendix (10 cm. long and 3 cm. in diameter) which was cooled by liquid air. This bulb was connected through a liquid air trap to a McLeod gage and a system for the quantitative analysis of small quantities of gas (of the order of one cubic mm.). Low pressures of mixtures of oxygen with either hydrogen or carbon monoxide were introduced into the bulb and the filament heated to a definite temperature. The products of the reaction, water vapor or carbon dioxide, were condensed in the appendix and thus prevented from returning to the filament. The pressures employed ranged from 0.1 up to 30 bars, so that the mean free path of the molecules was many times greater than the diameter of the filament. The velocity of the reaction was determined by taking readings of the gage at regular intervals.

[1] Jour. Amer. Chem. Soc., *38*, 1145, 1916.

[2] A preliminary account of these experiments, giving only qualitative results, was published in the Jour. Amer. Chem. Soc., *37*, 1162, 1915. The complete data on these experiments, together with that on several other similar reactions, will probably be published in the same journal.

With filament temperatures up to about 500–700° K., it was found that the reaction velocity increased rapidly with temperature. The rate was proportional to the partial pressure of oxygen, and *inversely proportional* to the pressure of hydrogen or carbon monoxide. Thus with an excess of oxygen the reaction started slowly, and as the proportion of combustible gas decreased, the rate increased until it became practically infinite (too rapid to measure). From this it may be concluded that hydrogen and carbon monoxide are negative catalyzers or catalytic poisons. Evidently these substances cannot prevent the reaction on the surface unless they are present on the surface. It thus follows that a surface of platinum at temperatures up to 500–700° K. in pressures of hydrogen or carbon monoxide, as low as one bar, is practically completely covered with an adsorbed film of these gases.

When the temperature of the platinum was raised, the reaction became so rapid that with a filament having a surface of 0.31 sq. cm., the pressure in the four liter bulb in some cases fell to half value in less than 6 seconds. To lower this rate a new filament (length 0.7 cm., diameter .003 cm.), having a surface of only .0067 sq. cm., was substituted for the old one. Under these conditions the velocity of the reaction could be followed up to the melting point of the filament.

With carbon monoxide the reaction velocity reaches a maximum when the filament temperature is about 900° K. and apparently becomes negligibly small in comparison, when the temperature is raised to 1300° K. or higher.

With hydrogen, the rate of reaction also reaches its maximum value at about 900° K. This rate does not decrease at higher temperatures, however, but remains practically constant up to the melting point of the filament.

From equation (1) the rate at which each gas comes into contact with the filament may be calculated. By comparing this with the actual rate at which the gas enters into reaction it is possible to determine ϵ. Out of all the hydrogen (or carbon monoxide) molecules which strike the afilment in a given time, let ϵ_1 represent the fraction which reacts with the oxygen. Similarly let ϵ_2 be the corresponding fraction for the oxygen molecules striking the surface. The following table gives the values of ϵ_1 and ϵ_2 calculated directly from the experimentally determined maximum rates of reaction.

In this table p_1 is the partial pressure of hydrogen or carbon monoxide in bars and p_2 is that of the oxygen. We see that when hydrogen is in large excess, 53 per cent. of all oxygen molecules which strike the filament react with hydrogen to form water. This may happen in either one of two ways:

Reaction $2H_2 + O_2 = 2H_2O$:

p_1	p_2	ϵ_1	ϵ_2
bars	bars		
20.0	4.2	.06	.53
1.3	11.5	.41	.09
Reaction $2CO + O_2 = 2CO_2$:			
12.6	0.7	.02	.18
1.4	0.7	.19	.20
1.4	12.0	.31	.02

1. The oxygen may react with hydrogen already present on the surface.

2. The oxygen may condense on the surface and react with hydrogen molecules which subsequently strike the surface.

In either case the reflectivity of the oxygen molecules cannot exceed 47 per cent. (100−53). Similarly we may conclude that the reflectivity of hydrogen molecules is not greater than 59 per cent.

The values for ϵ given in the above table are to be looked upon as lower limits. No correction was made for the cooling effect of the leads, which was very considerable with the short filament used. This correction would be much more important in the case of the combustion of carbon monoxide, since with this reaction the maximum velocity occurs only over a narrow range of temperature. Furthermore, traces of carbon dioxide were found to slightly poison the surface of the platinum, so that the catalyzer only slowly recovered its full activity. It may well be that minute traces of impurities have made the values of ϵ lower than they should be under ideal conditions.

From these considerations it seems probable that the values of ϵ corresponding to perfectly pure gases and a filament at uniform temperature, might approach unity as a limit in the case of each of three gases.

These experiments indicate that the reflectivity of oxygen, hydrogen, and carbon monoxide molecules is small even at temperatures of 900° K. There is every reason to believe that the reflectivity at room temperature is not greater than at higher temperatures.

A large number of other heterogeneous reactions are being studied by similar methods and the coefficients ϵ are being determined. All of this work so far seems to bear out the general conclusion that values of ϵ much less than unity occur only where the surface of the solid is largely covered by some inactive material. The velocity of the reaction is thus determined by that *fraction of the surface* which is active.

(*b*) *Homogeneous Reactions.*—Although homogeneous reactions furnish no direct evidence regarding the reflectivity of molecules from solid sur-

faces, yet several cases that have been studied have indicated that reactions are by no means rare in which *every* collision between unlike molecules *results in combination*. In this case we may consider that the reflectivity between the molecules is negligible, and are thus led to suspect that in many gas reactions, when two molecules collide, they stick to each other (condense), although they may subsequently separate again (evaporate).

When a tungsten filament is heated to 2800° K. in vacuum, it evaporates at the rate of 0.43×10^{-6} grams per sq. cm. per second.[1] If the filament is surrounded by nitrogen at a pressure less than 500 bars, the rate of evaporation remains unchanged, but each *atom* of tungsten vapor combines on its first collision with a nitrogen molecule to form the definite chemical compound WN_2, which collects on the bulb as a brown deposit. The nitrogen therefore disappears at the constant rate (independent of pressure) of .057 cubic mm. of nitrogen (at 1 megabar) per sec. per sq. cm. of tungsten surface. As the temperature of the filament is raised the rate of disappearance of nitrogen increases exactly in proportion to the rate of evaporation of the tungsten.

In a similar way it has been found[2] that tungsten atoms combine on the first collision with carbon monoxide molecules to form WCO, and that platinum atoms combine on the first collision with oxygen molecules to form PtO_2.

A remarkable case is that of molybdenum and nitrogen. There is definite evidence[3] that each collision between an atom of molybdenum and a molecule of nitrogen results in combination, but there are apparently two kinds of compound formed. One is a stable chemical compound which, when it deposits on the bulb, cannot be decomposed by heating to 350° C., while the other is an extremely unstable compound which decomposes spontaneously when it strikes the bulb. The stable compound tends to be formed in larger amount when the velocity of impact of the molybdenum atom and the nitrogen molecule is *small*; that is when either the bulb temperature or the filament temperature is low. On the other hand, a high velocity of impact (high temperature of bulb or filament) favors the formation of the unstable substance.

There are indications of a similar behavior when a tungsten filament is heated to a very high temperature (3000° K. or more) in hydrogen at low pressure, only in this case the compounds formed are less stable.

[1] Langmuir, PHYS. REV., *2*, 340, 1913.
[2] Jour. Amer. Chem. Soc., *37*, 1159, 1915.
[3] Jour. Amer. Chem. Soc., *37*, 1157, 1915.

II. Theoretical Considerations.

The phenomena of condensation, evaporation and reflection of molecules are closely related to those of the viscosity, heat-conductivity and adsorption of gases at low pressures.

Various hypotheses regarding the mechanism of these phenomena have been proposed. Maxwell[1] in considering the surface conditions of a gas in contact with a moving solid, assumed that " of every unit of area a portion f, absorbs all the incident molecules, and afterwards allows them to evaporate with velocities corresponding to those in still gas at the temperature of the solid, while a portion $(1 - f)$ perfectly reflects all the molecules incident upon it."

Smoluchowski[2] used a similar hypothesis in regard to the temperature drop near a surface in a gas at low pressure. He also suggested a second hypothesis, namely: When molecules of a temperature T_1 strike a surface at a higher temperature T_2, the molecules leaving the surface have a temperature T intermediate between T_2 and T_1 such that

$$T - T_1 = \alpha(T_2 - T_1), \tag{2}$$

where α is a number less than unity which has subsequently been called " accommodation coefficient " by Knudsen.

Smoluchowski considered that the same value of f or α could be applied to the phenomena of both viscosity and heat conductivity and thus calculated a relation between the coefficient of slip and the temperature drop at the surface.

Knudsen (*l. c.*), on the other hand, considered α to be unity in the case of viscosity, although not in the case of heat conduction.

Baule[1] attempts to solve this difficulty by analyzing the probable mechanism by which heat or momentum is transferred from gas to solid. Baule assumes that the solid consists of a cubic space lattice of elastic spherical molecules or atoms which are vibrating about their equilibrium positions with a mean kinetic energy corresponding to the temperature of the solid.

The molecules of the gas strike against those of the solid and rebound from them according to the laws of elastic collision. If E_1 be the mean kinetic energy of the incident molecules, E_2 the mean energy of the molecules of the solid, and E' the mean energy of the gas molecules after one collision with the molecules of the solid, then

$$E' = \beta E_1 + (1 - \beta)E_2, \tag{3}$$

[1] Phil. Trans., *170*, 249, 1879.

[2] Wied. Ann., *64*, 101, 1898; Wien. Sitzungsber., *108*, 5, 1899; Phil. Mag., *46*, 199, 1898.

[3] Ann. Phys., *44*, 145, 1914.

where

$$\beta = \frac{m_1^2 + m_2^2}{(m_1 + m_2)^2}. \tag{4}$$

Here m_1 is the mass of the gas molecules and m_2 is that of the molecules of the solid.

It is evident that many of the molecules make more than one collision before leaving the solid surface. Baule assumes that, of all the molecules striking the surface, the fraction ν make only one collision, while the fraction $1 - \nu$ are absorbed and thus make such a large number of collisions that they reach complete equilibrium with the solid before leaving it again.

Thus, if E is the mean energy of all the molecules leaving the surface we have

$$E = \nu E' + (1 - \nu)E_2, \tag{5}$$

whence from (3)

$$E = \beta\nu E_1 + (1 - \beta\nu)E_2. \tag{6}$$

Since the mean energy of molecules is proportional to their temperature Equation 6 may be written

$$T = \beta\nu T_1 + (1 - \beta\nu)T_2, \tag{7}$$

or

$$(T - T_1) = (1 - \beta\nu)(T_2 - T_1). \tag{8}$$

By comparing this equation with (2) it is seen that they are of the same form and that $(1 - \beta\nu)$ has the same significance as Knudsen's accommodation coefficient.

In a similar manner Baule calculates the coefficient of slip. Let v_1 be the average velocity component, parallel to the surface, of the incident molecules; v_2 the tangential velocity of the surface in the same direction, and v' be the average velocity (parallel to the surface) of the gas molecules which rebound from the surface after one collision. Baule shows that

$$v' = \gamma v_1 + (1 - \gamma)v_2, \tag{9}$$

where

$$\gamma = \frac{m_1}{m_1 + m_2}. \tag{10}$$

Of all the molecules striking the surface, the fraction ν make only one collision and are thus reflected with the velocity component given by (9), whereas the fraction $(1 - \nu)$ are absorbed and thus finally leave the surface with the average velocity component v_2. If v be the average velocity component parallel to the surface of *all* the molecules leaving it, then

$$v = \nu v' + (1 - \nu)v_2, \tag{11}$$

whence from (9)

$$v = \gamma\nu v_1 + (1 - \gamma\nu)v_2 \tag{12}$$

or

$$(v - v_1) = (1 - \gamma\nu)(v_2 - v_1). \tag{13}$$

The accommodation coefficient for viscosity is thus $(1 - \gamma\nu)$ instead of the $(1 - \beta\nu)$ which applies to heat conductivity. Thus Baule shows that there is no theoretical justification for Smoluchowski's assumption that the coefficients for heat conduction and viscosity are the same.

In the case of hydrogen in contact with a platinum surface we have $m_1 = 2$ and $m_2 = 195$, whence by (4) and (10), $\beta = 0.98$ and $\gamma = .01$. If we take Knudsen's value $\alpha = 0.26$ for the accommodation coefficient (heat conduction), we find $1 - \beta\nu = 0.26$, whence $\nu = 0.76$. From this we obtain $(1 - \gamma\nu) = 0.992$, which should be the accommodation coefficient for viscosity. This is in good agreement with Knudsen's experiments from which he concludes that the directions of the reflected molecules are independent of those of the incident molecules; in other words, that $\alpha = (1 - \gamma\nu) = 1.00$.

If we consider the case of argon in contact with platinum, for which Soddy and Berry found $\alpha = 0.85$, we obtain:

$$\begin{aligned} m_1 &= 40, \\ m_2 &= 195, \\ \alpha &= 0.85, \\ \beta &= 0.72, \\ \gamma &= 0.17, \\ 1 - \beta\nu &= 0.85, \\ 1 - \gamma\nu &= 0.965. \end{aligned}$$

The accommodation coefficient for viscosity thus decreases with increasing density of the gas, but remains nearly equal to unity.

The experimental work on slip has shown that the accommodation coefficient for viscosity is nearly unity, but the accuracy of the results has not yet been sufficient to determine whether the values calculated by Baule's theory are correct.

Baule attempts to calculate the coefficient ν by making various assumptions as to the manner in which the molecules on the surface are "shadowed" by others, but the validity of the assumptions seems so doubtful that the resulting equations have little more value than empirical equations.

On the whole, Baule's theory marks a distinct advance in our understanding of the mechanism of the exchange of energy between a gas and a solid, but closer consideration of the assumptions underlying Baule's theory shows that they cannot correspond to the facts.

Baule fails to take into account the attractive forces between the atoms, although it is evident that such forces must be of prime importance in determining the amount of condensation and reflection. The phenomena of cohesion, condensation and adsorption are all manifestations of these attractive forces, and Sutherland[1] has shown that even in the gaseous state the attraction between molecules considerably decreases their mean free path.

We know from the work of Bragg and others that the atoms of crystals are arranged according to a space lattice structure in which the identity of molecules usually disappears.

In a crystal of sodium chloride the forces holding the crystal together evidently act between adjacent sodium and chlorine atoms; in other words, they are of the nature of what we have usually called chemical forces. In a diamond crystal the carbon atoms form an endless chain of benzol rings, and the stability of this chemical group is probably the cause of the hardness, high melting-point and low vapor pressure of solid carbon. There is every reason to assume that all forces acting between the atoms of solid bodies are qualitatively of the same nature. The inert gases crystallize at low temperatures, so that even with these substances the atoms are surrounded by force fields which are only quantitatively different from those of more chemically active substances.

In the case of the diamond the arrangement of the atoms corresponds to the tetravalent character of the carbon atom, but in most crystals the valency of the atoms appears to be *divided* between several other atoms. Thus in the sodium chloride crystal the single valency of the sodium is divided between six chlorine atoms.

The principal characteristics of chemical forces are that they act only through very short distances and that they show in a marked degree the phenomena of saturation. Thus chemical forces act only between *adjacent* atoms, and even then only when the distances between the atoms are of the order of magnitude of the diameter of the atoms. When an atom of oxygen has taken up two hydrogen atoms it loses its attraction for other hydrogen atoms: it becomes chemically saturated. However, from the fact that water molecules become associated $(H_2O)_n$ and readily combine with substances as water of crystallization, we may conclude that the presence of two hydrogen atoms around an oxygen atom does not entirely saturated the chemical forces. Werner's theory of valence recognizes the existence of residual valences.

In a crystal the forces of attraction must be balanced by repulsive forces. We cannot assume that the repulsive forces are exerted only

[1] Phil. Mag., *36*, 507, 1893.

during collisions between adjacent atoms but, because of the work of Einstein,[1] Lindemann[2] and others, must assume that the atoms oscillate about positions of equilibrium in which the attractive and repulsive forces balance.

The atoms on the surface of a crystal must also be held by attractive and repulsive forces, so that they oscillate about equilibrium positions, but these atoms must be looked upon as being in an unsaturated state. There is every reason, therefore, for the existence of very strong attractive forces within a short distance of the surface of solid bodies. The phenomena of adsorption may be looked upon as a result of these unsaturated chemical forces. This will be discussed in more detail in Part II. of this paper.

By the aid of the viewpoint developed above, let us analyze more closely the probable mechanism of condensation, reflection and evaporation of atoms or molecules.

If an atom (or molecule) A approaches the surface of a solid body, it will be subjected to an attractive force as soon as it comes within a certain distance of the surface. This force will increase in intensity as A approaches nearer the surface, will pass through a maximum and will then decrease to zero when A reaches the equilibrium position. The work done by the attractive forces will have been converted into kinetic energy, part of which is possessed by the atom and the remainder of which is divided among atoms forming the surface.

The kinetic energy of A will carry it past the equilibrium position into a region in which it is subjected to a repulsive force. The component of its velocity toward the surface will thus decrease to zero. It will then be driven back through the equilibrium position, and if its outward velocity is sufficient it may escape from the region of attractive forces and travel indefinitely away from the surface. On the other hand, if its velocity is not great enough to enable it to escape, it will describe a complex orbit and, by loss of energy to adjacent atoms, will finally oscillate about its equilibrium position with a mean kinetic energy corresponding to the temperature of the surface.

The amount of work done by the attractive forces upon an atom A while it moves to an equilibrium position is measured by the heat of evaporation or adsorption and is equal to λ/N, where λ is the internal heat of evaporation per gram molecule and N is equal to 6.062×10^{23}. In the case of adsorption of a gas by a solid λ represents the heat of adsorption.

[1] Ann. Phys., *34*, 170, 1911, and *35*, 679, 1911.

[2] Phys. Ztschr., *11*, 609, 1910.

If the attractive and the repulsive forces were both exerted by a single atom of the solid, and if this atom could move freely towards the incident atom, then we should be justified in treating the problem as if attractive forces were absent and elastic collisions occured. In this case we could apply Baule's results directly.

But it is almost certain that the attractive forces are exerted by several atoms. Bragg has found that among metals the face centered cubic lattice structure is the most common. In this lattice each atom is surrounded by twelve others equally spaced from it. An atom on the surface must then usually have from four to eight other atoms exerting force on it. On the other hand, it is very probable that an atom which passes through the equilibrium position with high velocity would be subjected to repulsive forces exerted principally by *one* atom of the solid. This would naturally follow from the fact that the repulsive force must increase with the proximity to an atom much more rapidly than the attractive force decreases on receding from the equilibrium position.

In order to be able to estimate the magnitude of the effects produced by this difference in the origin of the attractive and repulsive forces, let us consider the case of the following model:

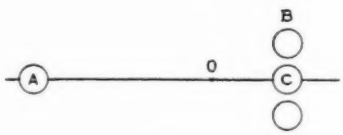


Fig. 1.

In Fig. 1, let A be an atom of mass m_1 which is attracted by a group of atoms B, each of mass m_2. Consider that all the atoms are elastic spheres initially at rest. Let O be the common center of gravity of all the atoms. Then the atoms will all move towards O. If we consider the one dimensional problem only, then we may assume that A will collide with *one* of the atoms B (say C) at the point O, and those two atoms will continue to move along the line AO. Let n be the number of atoms in the group B, excluding C, the one which collides with A. If V_1 and V_2 are the velocities (all measured from left to right) of A and C respectively just before their collision, and V_1' and V_2' are the velocities just after their collision, then we have by the principles of the conservation of energy and momentum:

$$m_1V_1^2 + m_2V_2^2 = m_1(V_1')^2 + m_2(V_2')^2, \tag{14}$$

$$m_1V_1 + m_2(1 + n)V_2 = 0, \tag{15}$$

$$m_1V_1 + m_2V_2 = m_1V_1' + m_2V_2'. \tag{16}$$

Let the ratio of the velocity of A before and after the collision be β, thus

$$\beta = \frac{V_1'}{V_1} \tag{17}$$

and let

$$\gamma = \frac{m_1}{m_2}. \tag{18}$$

If we substitute these in equations (14), (15) and (16) and solve for β, nd

$$\beta = \frac{\gamma n \pm (\gamma + n + 1)}{(n+1)(\gamma+1)}.$$

For the case in hand it can be readily seen that we should take the negative sign. Equation (19) thus becomes:

$$\beta = -\frac{1 + \gamma\left(\frac{1-n}{1+n}\right)}{1+\gamma}. \tag{20}$$

If $n = 0$, this gives $\beta = -1$, so that the atom A has its velocity reversed. Thus when $n = 0$ the existence of attractive forces between the atoms does not change the conditions from those of elastic collisions. If, however, $n = 1$ we find

$$\beta = -\frac{1}{1+\gamma},$$

so that the velocity after collision is much less than we would calculate according to the laws of elastic collision.

This loss in velocity, which Baule has failed to take into account, would result in a very great decrease in the number of atoms reflected from the surface. In order to estimate the effect on the reflectvity, we need to consider the initial velocity of the atom A, due to its thermal energy.

We may calculate this effect approximately by considering two atoms A and C having given initial velocities, but without attractive force between them. Let the initial velocities of A and C be v_1 and v_2 respectively. Let v_0 be the velocity of the common center of gravity of A and C and let v_1' be the velocity of A after collision.

Then

$$v_0 = \frac{m_1 v_1 + m_2 v_2}{m_1 + m_2} = \frac{\gamma v_1 + v_2}{\gamma + 1} \tag{21}$$

The velocity of A towards the center of gravity is $v_1 - v_0$ before collision. After collision this velocity is reversed. The actual velocity of A after collision v_1' is thus equal to $-(v_1 - v_0) + v_0$. This gives, with (21)

$$v_1' = \frac{\gamma v_1 + 2v_2 - v_1}{1+\gamma} \tag{22}$$

Let us now return to the consideration of an atom striking a surface toward which it is attracted. We have seen that the work done by the attractive forces in bringing the atom to an equilibrium position is λ/N. This appears as kinetic energy of the atom $\frac{1}{2}m_1V_1^2$. If M_1 is the molecular weight of the atom or molecule A, then since $M_1 = Nm_1$

$$V_1 = \sqrt{\frac{2\lambda}{M_1}}. \tag{23}$$

After collision with the atom C the velocity of A will be

$$V_1' = \beta\sqrt{\frac{2\lambda}{M_1}}.$$

But because of the initial velocities of A and C the velocity V_1' should be increased (approximately) by v_1', so that the velocity of A, upon returning to the equilibrium position, will be

$$\beta\sqrt{\frac{2\lambda}{M_1}} + v_1'.$$

The condition that the atom may just be able to escape from the surface is that this velocity shall be equal to $-\sqrt{2\lambda/M_1}$, in other words, the condition is

$$v_1' = -(1+\beta)\sqrt{\frac{2\lambda}{M_1}}. \tag{24}$$

Now let α_1 and α_2 be the ratios between the initial velocities of A and C respectively, and the mean velocities due to thermal agitation. Thus,

$$\alpha_1 = \frac{v_1}{\bar{v}_1} \quad \text{and} \quad \alpha_2 = \frac{v_2}{\bar{v}_2}, \tag{25}$$

where the mean velocities of thermal agitation $\bar{v}_1$ and $\bar{v}_2$ are given by

$$\bar{v}_1 = \sqrt{\frac{3RT_1}{M_1}} \quad \text{and} \quad \bar{v}_2 = \sqrt{\frac{3RT_2}{M_2}}. \tag{26}$$

Substitute (25) and (26) in (22), and the resulting value of v_1' in (24). Then substitute the value of β from (20), and remembering that $M_1/M_2 = \gamma$ we obtain our final equation:

$$\tfrac{1}{2}\alpha_1(\gamma - 1) + \alpha_2\sqrt{\frac{\gamma T_2}{T_1}} = -\frac{\gamma n}{n+1}\sqrt{\frac{2\lambda}{3RT_1}}. \tag{27}$$

This equation furnishes us an approximate method of estimating the effect of various factors upon the reflection of atoms from a surface. This will best be illustrated by a few examples.

First Case: $m_1 = m_2$.

In the first place, let us consider the case of a substance in equilibrium with its own saturated vapor. We then have $T_1 = T_2$ and $m_1 = m_2$, so that $\gamma = 1$.

If we express λ and R in calories ($R = 2$). then equation (27) reduces to

$$\alpha_2 = -\frac{n}{n+1}\sqrt{\frac{\lambda}{3T}}. \tag{28}$$

This equation tells us how large α_2 must be in order that the atoms of vapor may be reflected. In the case of tungsten at 3000° K., $\lambda = 206{,}000$ calories, so that we have

$$\alpha_2 = -4.8\frac{n}{n+1}. \tag{29}$$

The following table gives the values of α_2 corresponding to different values of n.

TABLE I.

n	α_2	P
0	0	0.50
0.1	−0.435	0.23
0.2	−0.80	0.08
0.3	−1.10	0.028
0.4	−1.37	0.0087
0.5	−1.60	0.0028
0.6	−1.80	0.00093
0.7	−1.97	0.00032
1.0	−2.40	17×10^{-6}
2.0	−3.20	14.0×10^{-9}
3.0	−3.60	1.0×10^{-9}

In this table n gives the effective number of atoms which attract but do not subsequently repel the incident atom. We have seen that there is good reason to believe that the attraction is exerted by three, four, or even more atoms, while the repulsion is exerted principally by one or two. We may therefore expect the value of n to be of the order of 2 or 3. The above table shows, however, that even if n should be as small as 0.1, reflection of the incident atom can occur only if it collides with an atom for which $\alpha_2 = -0.445$; that is, an atom which is already moving by its thermal agitation with a velocity component away from the surface equal to 44 per cent. of the mean thermal velocity. The column headed P gives the probability, according to Maxwell's distribution law, that any given atom on a surface should have a velocity in a given direction exceeding $\alpha_2\bar{v}_2$. Thus, according to the table, only 23 per cent. of the atoms on the surface have an outward velocity component greater than

44 per cent. of the mean velocity. The probability P is calculated by the equation

$$P = \frac{1}{\sqrt{\pi}} \int_{\alpha_2\sqrt{3/2}}^{\infty} e^{-x^2}\, dx. \tag{30}$$

With values of n as large as 2 or 3, the probability is negligibly small that an atom on the surface will have a sufficient velocity to cause the reflection of an incident atom.

The above calculations lead to the conclusion, which is in good accord with experimental facts, that the reflection of tungsten atoms from a tungsten surface takes place to a negligible degree only.

By equation (28) we see that the reflectivity of atoms from a surface will depend on the coefficient n and the ratio λ/T. It seems probable that n is of the same order of magnitude for all substances and has a value somewhere between 1 and 3. According to Trouton's rule the latent heats of evaporation of different substances are proportional to the absolute boiling points. Nernst finds that this rule is only approximate, and modifies it by placing the ratio λ/T proportional to log T. If we consider a series of different substances at " corresponding " temperatures the values of λ/T will not differ very greatly, but according to Nernst will be smaller the lower the absolute boiling point of the substance.

TABLE II.

Substance.	T_0	λ	λ/T	α_2	P
H_2.....	20.4	205	10.1	0.92	.055
O_2.....	90.	1,680	18.7	1.25	.015
H_2O.....	373.	9,000	24.1	1.42	.0069
Hg.....	631.	12,300	19.5	1.28	.013
Pt.....	4200.	109,000	26.0	1.47	.0054
Mo.....	3900.	160,000	41.0	1.85	.0007
W.....	5100.	200,000	39.0	1.82	.00085

Table II. contains data for a few substances. The absolute boiling point T_0 is given in the second column, while λ, the internal latent heat of evaporation at the boiling point, is given in the third. It is seen that the maximum range of the values of λ/T is only from 10 to 41, and, since this ratio in (28) occurs under the radical, the value of α_2 only varies within the ratio 1 to 2. The values of α_2 and P calculated by taking $n = 1$ are also given in Table II.

These data are calculated for the temperature of the boiling point. At lower temperatures α_2 would be larger so that P would be still smaller than the values given in the table.

In the above discussion we have derived a method of calculating the probability that an atom on the surface of a solid may have a sufficient velocity to cause an incident molecule to be reflected. The calculation was based, however, on the assumptions:

1. That the forces and motions involved are all normal to the surface.

2. That the collisions are perfectly elastic and that the work done on the incident particle by the attractive forces all appears as kinetic energy of this particle.

It is certain that the first assumption cannot correspond to the facts. The directions of motion of the incident particles after the collisions are probably distributed uniformly in all directions so that the chance of an atom being reflected is *very much* less than that given by P.

It is also probable that the second condition is not fulfilled, which must result in a still further decrease in the amount of reflectivity. Some idea of the rapidity with which adjacent atoms in a solid reach thermal equilibrium may be obtained from a consideration of the heat conductivity.

The problem is similar to that of a calculation of the " time of relaxation " for a gas. The distribution of velocities among the molecules of a gas in the steady state is given by Maxwell's distribution law. If a deviation from this law is brought about in some manner, and the gas is then left to itself, the distribution will rapidly return to that of Maxwell. The time required for the abnormal condition to subside is measured by the " time of relaxation," which Maxwell defines as the time needed for the deviation (measured in terms of kinetic energy) to fall to $1/e$th of its original value.

The following roughly approximate method will enable us to estimate the order of magnitude of the time of relaxation in a solid body.

Let us imagine that a single layer of atoms on the surface of a solid is at a temperature T, while the underlying layers of atoms are at zero temperature. If h is the heat conductivity of the solid, and σ is the distance between adjacent atoms, then the heat flowing between the first and second layers will be hT/σ per sq. cm. if we neglect the change in temperature of the second layer. The number of atoms in the surface layer will be $1/\sigma^2$ per sq. cm. and the heat capacity of each atom is $3k$, where k is the Boltzmann gas constant 1.37×10^{-16} erg./deg. We thus obtain

$$\frac{hT}{\sigma} = -\frac{3k}{\sigma^2} \cdot \frac{dT}{dt}, \tag{31}$$

or

$$ln \frac{T_0}{T} = \frac{h\sigma}{3k} t. \tag{32}$$

If we let T_0/T equal e, then t will become equal to the time of relaxation, which we may represent by t_r, thus

$$t_r = \frac{3k}{h\sigma}. \tag{33}$$

The times of relaxation for various substances as calculated by this equation are given in the fourth column of Table III. The data used in the calculation, h and σ, are given in the second and third columns. The values of σ were calculated from the density ρ and atomic weights A given in the fifth and sixth columns. For such substances as calcite and glass A was taken to represent the average atomic weight of all the atoms in the substance. The seventh column gives τ the natural period of oscillation of the atoms of the substance.

TABLE III.

Substance.	h erg/cm. sec.	σ cm.	t_r sec.	ρ g/cm^3.	A	τ sec.	$\frac{t_r}{\tau}$
	$\times 10^7$	$\times 10^{-8}$	$\times 10^{-15}$			$\times 10^{-15}$	
Copper	3.84	2.3	0.46	8.9	64.	180	.0026
Tungsten	1.25	2.5	1.3	19.	184.	170	.0077
Platinum	0.7	2.5	2.3	21.5	195.	210	.011
Mercury	.082	2.9	17.	13.6	200.	640	.027
Quartz	.09	2.3	20.	2.6	20.	186	.11
Rock salt	.06	2.8	25.	2.2	29.	250	.10
Calcite	.034	2.3	53.	2.7	20.	138	.38
Soda-glass	.01	2.4	170.	2.5	21.	200	.85
Ice	.004	2.2	470.	0.9	6.	370	1.3
Sulfur	.0026	2.9	550.	2.1	32.	460	1.2
Paraffin	.0025	2.0	790.	0.9	4.6	440	1.8

This natural period is the reciprocal of ν the atomic frequency (Eigenschwingungen). The atomic frequency may be calculated in any one of a half dozen different ways[1] with substantially similar results. The values given in the table have been obtained from the compressibilities K by means of Einstein's[2] equation

$$\tau = \frac{1}{\nu} = 3.5 \times 10^{-8} A^{\frac{1}{3}} \rho^{\frac{1}{3}} K^{\frac{1}{2}}. \tag{34}$$

Objections may be raised against the use of this equation for the calculation of the periods of oscillations of the atoms of compounds, but it is not likely that the order of magnitude of the result will be in error. Koref[3] calculates by other methods that in a rock salt crystal the fre-

[1] Harkins and Hall, J. Amer. Chem. Soc., *38*, 207, 1916.

[2] Ann. Phys., *34*, 170, 1911.

[3] Phys. Ztsch., *13*, 186, 1912.

quency of the sodium atom is 6.8×10^{12} and that of the chlorine is 5.5×10^{12} The atomic frequency calculated from the value of τ in Table III. is 4×10^{12}, which is not greatly different from Koref's results.

The last column of the table gives the ratio of the time of relaxation to the natural period of oscillation of the atoms. In the case of the metallic substances this ratio is very much less than unity, which must mean that thermal equilibrium is established between adjacent atoms in a small fraction of the time necessary to complete a single oscillation.

Under these conditions it is apparent that our second assumption (elasticity in collisions) is not justified in the case of metals. It is probable, in fact, that atoms of metal vapor striking the surface reach practically perfect thermal equilibrium with adjacent atoms before they can possibly escape again from the surface. The amount of reflection during the condensation of metallic vapors is therefore probably extremely small. Since the high heat conductivity of metals is related to their electrical conductivity, we may conclude that "free electrons" play an important part in the mechanism of the condensation of metallic vapors.

From Table III. we see that even in the substances of low heat conductivity such as ice or sulfur, the "rate of relaxation" is so high that the collisions must be far from elastic. A slight loss of energy to adjacent atoms, must have a very great effect in decreasing the chance that an incident atom or molecule will be able to escape, so that even with non-metallic substances it is probable that the reflection of molecules occurs to a much smaller degree than would be estimated from the values of P given in Table II.

However, it would not be safe to conclude that in all cases where molecules strike similar molecules (or atoms) on a surface that the reflectivity must be negligibly small. We have seen that there is evidence that metals in contact with hydrogen even at low pressures have their surface completely covered with a layer of hydrogen atoms or molecules. The accommodation coefficient 0.25 observed for hydrogen in contact with platinum, indicates that a considerable fraction of the hydrogen molecules striking other hydrogen atoms or molecules on the surface is reflected. The reasons for the high reflectivity in this case probably are:

1. The heat of condensation λ is very small. By Table II. we see that λ for liquid hydrogen at its boiling point is only 205 calories per gram molecule. It is probable, however, that the hydrogen atoms on a metal surface are held by very strong chemical forces[1] so that they are much

[1] There is reason to think that for the condensation of the first layer of atoms of hydrogen on platinum the value of λ is about 40,000 calories per gram molecule.

more thoroughly saturated than the atoms or molecules in liquid hydrogen. There is good reason to think, therefore, that such a layer of hydrogen atoms would exert only very weak attractive forces on incident hydrogen molecules, and that the value of λ for the condensation of the second layer would be much less than 205 calories.

We see by equation (28) that a small value of λ would tend to increase the number of atoms reflected.

2. The temperature is very high compared to the boiling point of hydrogen, and this fact, according to (28) and (30), would tend to increase the chance of reflection. It may also decrease λ. Although the heat of evaporation of liquids decreases to zero when the critical temperature is reached, we must not consider that λ also disappears at this temperature. In the sense in which we are using this quantity it represents the work done in separating the atoms of the solid or liquid to an infinite distance from each other. This quantity evidently may have considerable values even at temperatures much above the critical temperature.

3. The atoms forming the adsorbed layer on the surface may be so rigidly held by the underlying metal as to greatly increase the tendency for the weakly attracted incident atoms to be reflected. In deriving equation 28 it was assumed that during the time of a collision, the atom on the surface is free to move according to the usual laws of elastic collisions. If the adsorbed atoms are rigidly held to the metal atoms the effective mass of the adsorbed atoms would be greatly increased. According to equation (27), this would tend to increase the reflectivity.

Another effect produced by the close coupling of the adsorbed atoms to the metal and the loose coupling to the incident atoms is to lengthen the time of relaxation of the incident atoms.

Second Case. Unlike Atoms.—So far, we have considered the condensation of a vapor on a solid whose surface consists of the same kind of atoms. If atoms of a light gas strike the surface of a solid consisting of heavy molecules, the case becomes more complicated, since we must use equation (27) instead of (28). Let us consider the case of hydrogen molecules striking an absolutely clean surface of tungsten or other heavy metal. For such a case we may put approximately $\gamma = .01$, so that, if we place $T_2 = T_1 = T$ and $R = 2$, equation (27) becomes

$$\alpha_2 - 4.95\,\alpha_1 = -0.058\frac{n}{n+1}\sqrt{\frac{\lambda}{T}}. \tag{35}$$

From this equation we may estimate the amount of reflection which would occur if the directions of all motions and forces were normal to the surface. Under actual conditions the amount of reflection would

be considerably smaller. In making this calculation we substitute in (35) the value of n, λ, and T and then choose particular values of α_1, and find α_2 by the equation. Thus if we place $n = 1$ and $\lambda = 40{,}000$, we find the pairs of values of α_1 and α_2 given in the first two columns of Table IV.

TABLE IV.

α_1	α_2	P_1	P_2
+0.	−0.34	1.00	0.28
+0.1	+0.15	0.98	0.60
0.2	+0.65	0.94	0.87
0.3	+1.14	0.87	0.98
0.4	+1.64	0.79	1.00
0.5	+2.14	0.69	1.00
1.0	+4.61	0.22	1.00

The value of α_2 gives the maximum (positive) velocity which an atom of the solid may have and still cause the reflection of an atom colliding with it. Thus from the table we see that if a molecule of hydrogen (A) starts from rest ($\alpha_1 = 0$) and is attracted towards the metal surface, it will only be reflected if the metal atom which it strikes is moving *towards* it with a velocity numerically in excess of that corresponding to $\alpha_2 = 0.34$. If, however, the hydrogen molecule starts with an initial velocity (normal to the surface) corresponding to $\alpha_1 = 0.1$ we see that it may be reflected even if it strikes a metal atom moving *away* from it with a velocity as large as that corresponding to $\alpha_2 = 0.15$.

The probability that a molecule striking the surface should have a velocity greater than α_1 is given by

$$P_1 = e^{-\frac{3}{2}\alpha_1^2}. \tag{36}$$

On the other hand, the probability P_2 that a molecule on the surface should have a velocity component less than that corresponding to α_2 may be readily calculated by means of equation (30). The probabilities P_1 and P_2 have been entered in Table IV. From these data we see for example, that 87 per cent. of all the incident molecules have velocities towards the surface greater than that corresponding to $\alpha_1 = 0.3$. In order that these molecules may be reflected it is necessary that α_2 shall not exceed 1.14, but according to the fourth column we see that 98 per cent. of the metal atoms have a value of α_2 less than 1.14.

From these data by approximate integration of $\int P_2 dP_1$, it can be shown that of all molecules striking the surface 97.3 per cent. would be reflected if we could assume all motions and forces to have directions

normal to the surface. This figure gives us an upper limit for the amount of reflection. This result is not greatly different if we take other values for λ or n. Thus if we take λ or n (or both) equal to zero, we obtain in a similar manner to that used above, the value 98.7 per cent. for the maximum possible reflectivity. On the other hand if we take $n = \infty$ and $\lambda = 40{,}000$ we find 95.1 per cent.

In many chemical and physical problems it is important to know how closely the reflectivity can approach 100 per cent. Thus in calculating the vapor pressure from the rate of evaporation, we made use of $(1 - r)$. (See equation (1).) In this case, where $\gamma = 1$, we have seen that we may always place $r = 0$. Similarly in estimating the velocity of a chemical reaction we may use an equation similar to (1) in which we use ϵ in place of $(1 - r)$.

In studying the mechanism of such reactions we need to know the order of magnitude of $1 - r$. Thus suppose in a given case we find that only one molecule reacts out of every thousand striking the surfaces, that is $\epsilon = 0.001$. In interpreting this result we need to know whether it is possible that 99.9 per cent. of the molecules are actually reflected.

From the calculations given above, it appears that the reflectivity can in no case exceed 99 per cent., and must in all probability be much less than this. Therefore a value of ϵ as small as .001 must be accounted for in some other way than by reflectivity, as for example by assuming that the greater part of the surface is covered with a material on which the given reaction does not take place.

The smallest accommodation coefficient that has been observed is 0.19 (hydrogen). This corresponds according to Baule's theory (equation 8), to a reflectivity of about 83 per cent., a value which is in reasonable agreement with the upper limit of 95–99 per cent. calculated above.

It thus seems extremely probable that when gas molecules strike solid bodies in no case are more than 90 per cent. of the molecules reflected.

RESEARCH LABORATORY,
GENERAL ELECTRIC COMPANY,
SCHENECTADY, N. Y.

(To be continued.)

THE MECHANICAL EQUIVALENT OF LIGHT AS DETERMINED FROM THE BRIGHTNESS OF THE BLACK BODY.

BY HERBERT E. IVES AND E. F. KINGSBURY.

1. INTRODUCTION.

THE brightness of any radiating body is represented by the general expression

$$b = \frac{1}{m\pi}\int_0^\infty J_\lambda L_\lambda d\lambda,$$

where

b = brightness, in candlepower per unit area.

J_λ = rate of energy emission by the radiator for the wave-length interval $d\lambda$, at the wave-length λ, in watts per unit area.

L_λ = the luminosity of the equal energy spectrum at any wave-length, in terms of $L_{\lambda\,max} = 1$.

π = factor transforming total (hemispherical) radiation, to radiation per steradian.

m = the mechanical equivalent of light (watts of luminous flux per lumen).

On interchanging b and m, a formula is obtained for the determination of the mechanical equivalent of light from brightness observations on a radiator whose radiating constants are known, *e. g.*, the black body.

In order for this method to be of value certain requirements must be met, in part purely physical, in part photometric, as follows:

Physical Requirements.—The condition controlling the emission of energy, *e. g.*, temperature, must be subject to accurate measurement. The relation between the controlling conditions and the resultant radiation must be accurately known, as for instance by a formula like the Planck equation: The values of the constants entering into this relation must be well established.

Photometric Requirement.—An absolutely essential condition is that the photometric method used to determine the brightness of the radiator shall be in exact agreement with the luminosity curve used in the calculation formula.

The objects of the present paper are, (1) to make a critical study of this method of obtaining the mechanical equivalent of light, when the

black body is used as the radiator; (2) to review certain published researches where this method has been used; (3) to outline the experimental procedure which should be adhered to; (4) to give certain new experimental data.

2. THE RELATION BETWEEN BLACK BODY BRIGHTNESS AND THE MECHANICAL EQUIVALENT OF LIGHT.

The radiation of the black body (J_λ) is according to our present knowledge best represented by the Planck equation, although it should be noted that this expression has never been exhaustively tested in the visible spectral region for high temperatures. The luminosity curve (L_λ) of the equal energy spectrum has been determined by the present writers from an extensive series of visual and physical photometric researches.[1] This curve is accurately represented by an equation recently published,[2] which can be readily combined with the Planck equation, to yield the brightness in the manner above indicated.

In order to incorporate the black body constants in their most usually published form, and for clearness of representation, the complete black body brightness equation may be written as follows:

$$b = \frac{1}{m}\,\frac{\sigma K^4}{\pi}\left[\frac{\int^{\infty} L_\lambda J_\lambda d\lambda}{\int_0^{\infty} J_\lambda d\lambda}\right]$$

where, in addition to the constants already given,

σ = the Stefan-Boltzman constant, connecting temperature and total emission.

K = absolute temperature.

The part within brackets is the *luminous efficiency*.

Fig. 1, reproduced in part from the paper describing the luminosity curve equation (2) shows not only the various component parts of the equation just given, but by the additional dotted and dashed lines exhibits certain inconsistencies and errors which are to be carefully watched against in its use. Thus the dashed line close to the light watts curve shows the result on the calculated light watts of using another luminosity curve which lies as a whole more toward the blue end of the spectrum. It not only is lower on the diagram, but its general slope is steeper than the one resulting from our luminosity curve. Were the mechanical equivalent determined by reference to an experimentally fixed point,

[1] See "Physical Photometry with a Thermopile Artificial Eye," Ives and Kingsbury, PHYS. REV., Nov., 1915, p. 319.

[2] "A Spectral Luminosity Curve and its Use," Kingsbury, PHYS. REV., Feb., 1916, p. 161.

on which several experimenters could agree, whatever their methods of colored light measurement, say at 2,000 degrees, this constant would be different depending on which luminosity curve was used. This is shown by the different distances between the light watts and the candlepower curves, this distance being the logarithm of the mechanical equivalent.

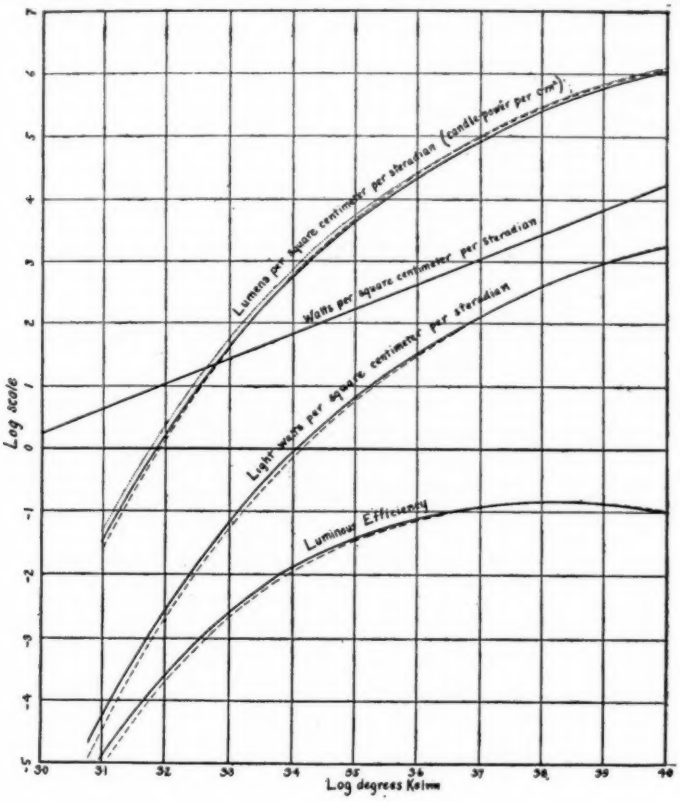

Lumens per square centimeter per steradian (candlepower per cm²)
Watts per square centimeter per steradian
Light watts per square centimeter per steradian
Luminous Efficiency
Log scale
Log degrees Kelvin

Fig. 1.

Light and power relations in the black body. Calculations on basis of $\sigma = 5.65 \times 10^{-12}$, $c_2 = 14{,}370$. Full lines representing light quantities are obtained by using Kingsbury luminosity curve equation, and experimental value of .00159 for the mechanical equivalent of light. Dashed lines show consequence of using wrong luminosity curve equation. Dotted line shows consequence of using right luminosity curve but wrong value of mechanical equivalent.

The candle power curve is here obtained by using the value .00159 for the mechanical equivalent of light, as obtained by us in other experiments.[2, 1] The dotted curve near the candlepower curve shows the consequence of using the wrong value of the mechanical equivalent with

[1] "The Mechanical Equivalent of Light," Ives, Coblentz and Kingsbury, PHYS. REV., April 1915, p. 269.

the right luminosity curve. The calculated and observed brightness points would lie on parallel but not coincident curves.

It should be clear from this diagram that no valid calculation of the mechanical equivalent of light can be made in the manner outlined unless the method of photometry employed is consistent with the luminosity curve assumed in calculating the light watts from the black body.

This is exactly as important as the agreement of the meter sticks or thermometers employed by separated laboratories working on a common problem.

The curves in Fig. 1 are calculated for the values 5.65×10^{-12} for σ, and 14,370 for c_2. The effect of a different choice of these constants within the limits of their present experimental uncertainty is quite large. The mechanical equivalent of light as calculated from black body brightness varies directly as σ, the experimental value of which has been until recently as much as 10 per cent. in doubt. The effect of a different choice of c_2 is exhibited in Figs. 4 and 6. The present uncertainty in the value of this constant, namely the range from 14,200 to 14,500, corresponds to 15 or 20 per cent. uncertainty in the value of "m." (It is therefore quite important in comparing results by different workers in this field to reduce the published results to the same figure for c_2.)

It should be evident from this study that even when the photometric part of the work meets the essential requirements above emphasized, a considerable uncertainty remains on the purely physical side. As a consequence the method cannot be expected to give as yet an accurate value for the mechanical equivalent of light. It should however give an excellent check on the order of magnitude of this constant, and offers a mode of approach independent of the particular radiation standards used in our earlier experimental work.

3. An Examination of Some Recently Published Experimental Work.

The method just outlined has been used recently by Pirani and Miething[1] and by Meyer[2] to determine the mechanical equivalent of light, although that constant does not appear in their papers under that name. It is however obtained from their data by simple multiplication and division. Their figures are both in the neighborhood of .0012, or considerably lower than our experimental value of .00159.

Now in both investigations the black body brightness values obtained

[1] "Strahlungsenergie, Temperatur und Helligkeit des Schwarzen Körper," Pirani and Miething, Verh. d. D. Phys. Ges., 13, p. 219, 1915.

[2] "Der Schwarze Körper als Lichtquelle im Temperaturbereiche von 2,000 bis. 10,000 abs," A. R. Meyer, Verh. d. D. Phys. Ges., 21, p. 383, 1915.

by Lummer and Pringsheim[1] are used. On examining these data we have found that they are not consistent with the luminosity curve used by the writers quoted and hence conflict with the essential photometric requirement.

In Fig. 2 is reproduced the brightness curve of the black body as cal-

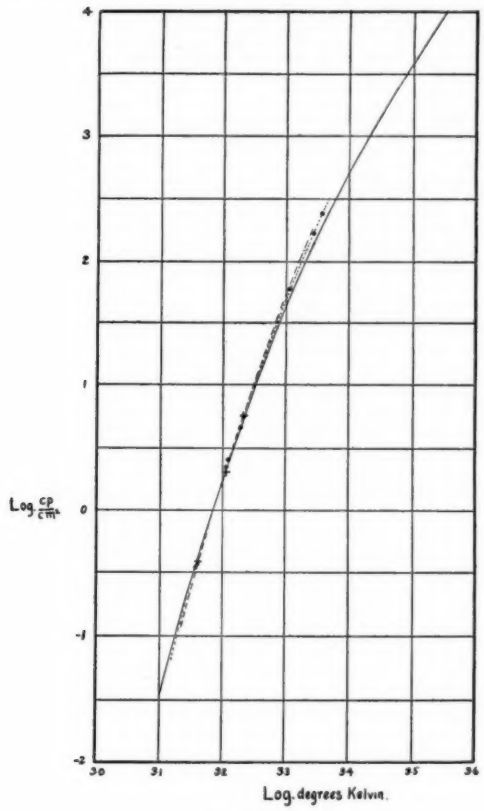


Fig. 2.

Black body brightness observations by Lummer and Pringsheim (crosses), and by Nernst (circles). Full line = values calculated from our equations and constants.

culated with the constants given above. On this we have plotted as small crosses the experimental values of Lummer and Pringsheim, and also the similar data obtained by Nernst,[2] as small circles.

It is evident that the experimental values scatter on both sides of the calculated to such an extent that they offer conclusive proof neither for nor against the mechanical equivalent value used to make the cal-

[1] "Temperaturbestimmung mit Hilfe der Strahlungsgesetze," Lummer and Pringsheim, Phys. Zeit., 3, 97, 1901.

[2] "Über die Helligkeit Glühende Schwarzer Körper," Nernst. Phys. Zeit., 7, p. 380, 1906.

culations. On analyzing the data however two points of significance appear. First, neither set of points follow the curvature of our line. Second, the deviation is of such a character that the lower points as a whole call for a higher value of the mechanical equivalent of light, than our experimental one, the higher points for a lower one.

These facts are clearly exhibited by Fig. 3, which shows the value of

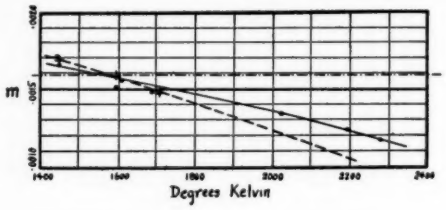


Fig. 3.

The mechanical equivalent of light as calculated by combining observations of Lummer and Pringsheim (crosses and dashed line), and Nernst (circles and full line) with our luminosity curve. Value varies with the temperature, showing non-agreement of photometric work with assumed luminosity curve.

the mechanical equivalent as calculated by using their observations in combination with our luminosity curve. If their visual observations were made by observers or photometric method in agreement with our luminosity curve, all the observed points should yield the same value of m, that is, should lie along a line parallel to the axis of abscissae. Instead they lie on lines at considerable angles to this axis.

Another mode of representing the extent of this deviation is obtained by finding that single wave-length which best represents the behavior of the total light in these observations. Thus the results of Lummer and Pringsheim are represented by a "Crova" wave-length of .542 μ; those of Nernst by wave-length .565 μ (shown by dotted lines in the figures). Now in this same region the Crova wave-length which corresponds to our luminosity scale is .58 μ.[2] This shows (assuming the validity of the Planck equation) that the photometric work of these observers corresponds to low illumination conditions, since our own in all referred to a definite high intensity condition. The equivalent wave-length of Lummer and Pringsheim's work is in fact so short as to correspond to twilight vision, where the Purkinje effect is dominant. In order to arrive at a value for the mechanical equivalent of light by the use of either of these sets of data a definition of "light" would have to be adopted fixed by a very different luminosity curve than that used by us, and furthermore, quite different depending on which set of data was used. Now Pirani and Miething, and Meyer, used Lummer and Pringsheim's data

with the luminosity curve determined by Ives,[8] which, for the temperatures in question is nearly identical with the curve represented by the Kingsbury equation. *They arbitrarily selected extrapolated points on the Lummer and Pringsheim curve*, the former choosing the point where the Hefner candlepower per square centimeter was unity, the latter the 2000-degree point (these points happen to be not far apart), and so arrive at their values near .0012 for *m*. Using the same data, however, with a different arbitrary selection of starting point, they could have obtained equally valid figures up to .0017, if they confined themselves to the region of actual experimental candlepower determinations, and indefinitely higher or lower figures according to how far they carried the extrapolation process.

Any attempt to determine the mechanical equivalent of light without first establishing the agreement of the photometric work with the assumed luminosity curve is a waste of time. In the absence of experimental data made on any consistent luminosity scale, in particular on the luminosity scale which we have developed in our photometric researches, it was evident to us that no further progress along this line could be made without a new experimental determination of black body brightnesses. We therefore decided to undertake this by an experimental photometric method previously proved to be in agreement with the luminosity curve as above used.

4. Experimental Work.

(*a*) *Distinctive Feature of Method.*—The one part of our determination of black body brightness which introduced any new procedure was the photometric method. Its characteristic feature was that every photometric observation was made at an exact color match. A large carbon (100-candlepower stereopticon) incandescent lamp was used as the comparison light, and this was always set at such a voltage as to give the condition of no color difference in the photometric field. The evaluation of the candlepower of this lamp was then made a separate experiment. By this means all our observations were placed on the chosen high intensity condition scale, to which our luminosity curve corresponds, even though many of the actual readings had to be made at very low illuminations.

The calibration of the comparison lamp could have been done on our physical photometer[1] whose wave-length sensibility is identically the luminosity curve by which the calculations in this paper have been made, thus in a concrete manner insuring that exact correspondence of photo-

[8] "The Spectral Luminosity Curve of the Average Eye," Ives, Phil. Mag., Dec., 1912, p. 853.

metric method and luminosity curve whose necessity has been emphasized. Actually for reasons of convenience, the calibration was done by means of the Fabry yellow solution recently described[1] whose transmission has been accurately determined by our visual photometric method. Inasmuch as the calibration of this solution by the physical photometer agrees with the visual calibration, and was in fact one of the tests by which the physical photometer was developed, the result is the same as though the physical photometer had been used. Parenthetically we may remark that there appears to be no way of guaranteeing that visual photometric results are consistent with a given spectral luminosity curve short of going through the process, as we have, of developing a physical photometer whose readings agree with the chosen visual method, and whose wave-length sensibility can be accurately determined.

(*b*) *Furnace Observations.*—The first series of measurements, extending over a temperature range from 1300 to 1500 degrees absolute, were made on a smell nichrome wound alundum tube electric furnace, of 20 centimeters' length, and 3 centimeters' internal diameter. This was furnished with several ring diaphragms to insure blackness, and the thermocouple, with which temperatures were measured, was imbedded in an alundum plug, blackened with iron oxide, at the center of the tube. This plug, with the thermocouple junction and the double-channelled porcelain tube immediatly surrounding the couple, formed the effective radiating surface, which should of course be perfectly black. When the furnace was in operation it was only with the closest attention, that any irregularities of brightness could be detected at this point, showing the blackness to be very good.

In front of the open end of the tube was placed a sheet metal screen with a round opening of half a square centimeter area. This formed the effective light source for the Lummer-Brodhun photometer head, 50 centimeters away. From the position of the photometer head the only part of the furnace interior visible was the plug described above. Between readings the sheet metal screen (which was fastened to a block of metal of large heat capacity) was moved away from the furnace to prevent overheating.

All the temperatures obtaind lay well within the range of a platinum platinum-rhodium thermocouple. Partly for convenience, and partly also because any optical method of temperature measurement would be begging the question of the validity of the Planck equation, temperatures were measured with the thermocouple. The instrument used was made by Heraeus, and was calibrated immediately before by the Bureau of Standards. The E.M.F. was read by potentiometer.

The experimental procedure was to very slowly raise the temperature from step to step, making a set of ten photometric readings at each approximately constant condition, before and after which temperatures were read. The mean value of the temperature during the photometric settings was ascribed to the mean photometric reading. As mentioned above, the voltage of the comparison lamp was always adjusted to give a color match with the furnace, and a separate measurement afterwards with the Fabry yellow solution fixed the corresponding candlepower.

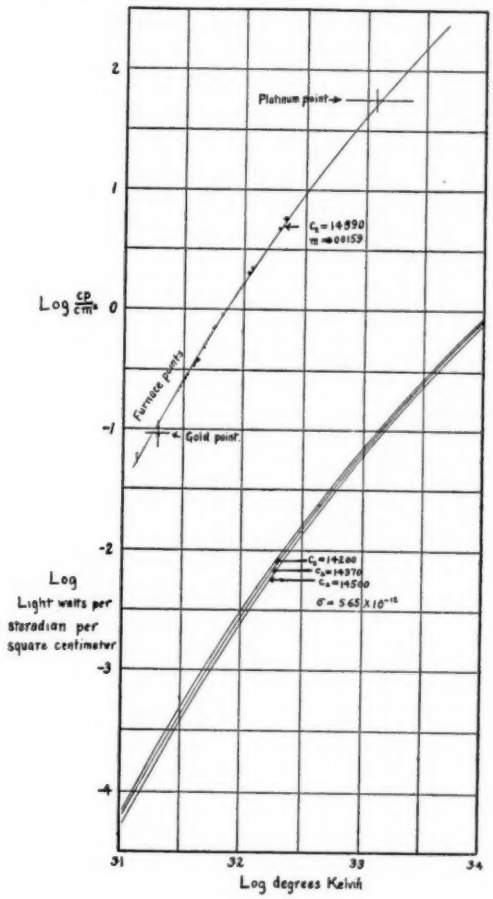


Fig. 4.

Experimentally obtained black body brightness, from furnace, gold and platinum. Data of Lummer and Pringsheim and Nernst shown by crosses and circles.

Measurements were made on this furnace up to the point where it burnt out, at about 1500 degrees absolute. The 23 brightness observations obtained on the furnace are plotted by dots in Fig. 4. They fall

very satisfactorily along our calculated curve plotted with the constants—

$$\sigma = 5.65 \times 10^{-12},$$

$$c_2 = 14{,}390,$$

$$m = .00159.$$

They will be further discussed after the description of the experimental work on metal wedge melting points.

(*c*) *Observations on Wedge-shaped Platinum Cavities.*—The second series of measurements were made on a black body at the melting point of platinum. For the construction of this furnace we availed ourselves of the scheme described by Mendenhall,[9] namely the use of a wedge of the metal heated electrically to its fusion point. The wedges were of pure platinum furnished by the American Platinum Company, 7.5 cm. long, 2.5 cm. wide of a thickness of .005 cm. The angle between the sides was made 10 degrees, this, as shown by Mendenhall being small enough to insure practically perfect blackness of the cavity.[10] The arrangements for holding the wedges were closely the same as those published by Mendenhall, except that the lower clamping piece was immersed in mercury instead of being fixed. The height of the mercury in its cup was carefully adjusted so that the platinum wedge was subjected to a minimum of strain at the fusing point. Heating was done by alternating current from the low voltage side of a Northrup furnace transformer.

Directly in front of the wedge was a heavy brass plate on which was fastened a carefully made slit of invar, 1.0 × 0.1 cm. in opening.[11] Invar was used to avoid the necessity of corrections for expansion due to heating which would have been hard to determine. The apparatus as used is shown in Fig. 5.

The technique of carrying the metal up to its melting point while keeping the photometer accurately set was learned by experiments on nickel wedges, which, however, because of the formation of oxide, were not satisfactory themselves for fixing a point on the curve. The final practice was obtained on two of the six platinum wedges which had been secured. The important point is to be sure that the wedge hangs exactly behind the slit when warmed up almost to the melting point, and is

[9] "Emissive Power of Wedge-shaped Cavities and their Use in Temperature Measurements," C. E. Mendenhall, Astrophysical Journal, 33, p. 91, March, 1911.

[10] It is possible that a chemically deposited coating of platinum black would give additional guarantee of blackness.

[11] Were we planning to do the work over we could make this slit only half as long, as there would still be plenty of light (with platinum) and there would be no doubt about the uniformity of temperature of the wedge over the whole length of the slit.

sufficiently wide open to fill the slit. Several preliminary heatings, of increasing intensity, are desirable, and when the metal is well annealed the wedge may be pulled open if necessary, while glowing and soft. In order to insure that the melt occurs exactly in front of the slit the edges of the wedge should be cut away slightly for a length a little more than that of the slit. The apex of the wedge should be pinched tightly together in the region near the slit to avoid the occurrence of a narrow strip of imperfect blackness down the center. Using the precautions just described, four wedges were melted with very satisfactory results, as far as definiteness and consistency are concerned. The photometric work was particularly satisfactory in that there is no detectable color

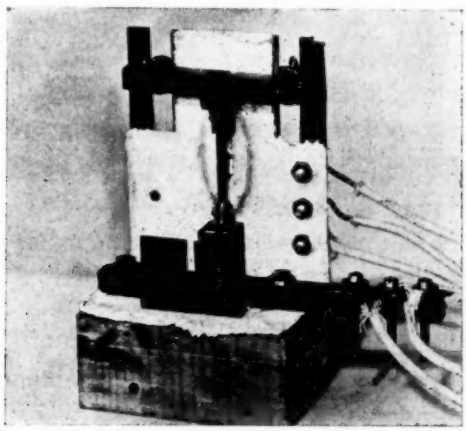


Fig. 5.

Apparatus used for metal wedge black bodies.

difference between the black body at this temperature and the regular "4-watt" carbon standards. The values obtained from these four melts were 58.2, 58.2, 58.5, and 58.5 candlepower per square centimeter, giving as our mean result 58.35.

The melting temperature of this platinum was accurately determined for us by the Bureau of Standards, as 2028 degrees Kelvin. The candlepower obtained is plotted at this temperature in Fig. 4. It will be seen that this does not lie on the calculated curve obtained by using the previously found mechanical equivalent figure. Using again the probable values, 5.65×10^{-12} for σ, and 14,390 for c_2, the mechanical equivalent of light works out from our platinum observations as .00139.

(*d*) *Observations on Gold Wedges.*—In the effort to trace the cause of the discrepancy between our furnace and platinum observations, we have tried to determine the palladium and gold points by the wedge method.

Our experiments with palladium were very unsatisfactory as it did not appear to possess a clear-cut melting point. With gold we were successful, but here the excessively low illumination of the photometer field from the .1 cm.^{2} aperture greatly lowered the photometric precision. The procedure was the same as with the platinum, except that the comparison lamp was run at a much lower voltage (decided upon from the furnace work), to secure color match. The four melts gave .086, .092, .0905 and .1031 as the candlepower per square centimeter at the melting temperature of our gold, with a mean figure of .0929. This temperature was determined for us by the Bureau of Standards as 1344 degrees Kelvin. Using the same values as before for the black body constants the mechanical equivalent of light is .00195. The mean candlepower is plotted with the others in Fig. 4.

5. Discussion of Results.

In Fig. 5 we have plotted the values of the mechanical equivalent of light as obtained from the 23 furnace observations, the four gold observations and the four platinum observations, using values of c_2 from 14,200 to 14,500, σ being taken as 5.65×10^{-12}. This plot is of interest in showing how greatly the choice of a value for this constant affects the value of m. It shows as well that no reasonable value of c_2 can be assumed which would, with an appropriate value of m, eliminate the discrepancy between the various sets of observations. The dashed line shows our previous experimental value .00159. It happens to be very nearly the average of the black body figures for the most likely values of the radiation constants.

Our efforts to find the cause of this discrepancy between the various black body figures have not met with success. It might be expected to lie either in lack of agreement between the photometric observations and the luminosity curve assumed, or in the determinations of temperature.

The former possibility is ruled out, in the case of this work, by the preliminary exact check of the visual and physical photometric methods, in the latter of which the luminosity curve here used is embodied. We have furthermore confirmed the fact that the error does not lie here by reducing the whole set of observations to their value as carried out by monochromatic red light and monochromatic green light, for which no question of choice of luminosity curve enters. To do this it was only necessary to evaluate the comparison lamp on the photometer, against the standard at its various voltages, through monochromatic glasses over the eyepiece. The equivalent wave-lengths of these glasses were

then found with the aid of the spectro-photometer,[12] thus giving the slopes of the isochromatic straight line plots of log. intensity against $1/K$. Lines drawn with these slopes through the platinum point did not pass through the gold point, and vice versa, the error being as large as by the total light method, thus showing that the trouble is connected with the temperature measurements.

In regard to the furnace measurements, we have, at the suggestion of Mr. Paul D. Foote, of the Bureau of Standards, returned the thermo-couple used to the Bureau, to have it tested for lack of homogeneity. Such a defect was found to exist. Most unfortunately however the correction suggested by the bureau for the actual depth of immersion of the couple, instead of decreasing the discrepancy, increases it. In view of the uncertainty as to when the inhomogeneity was introduced, we are forced to accord small weight to the furnace observations.

The greatest discrepancy however—that of 30 per cent., between the gold and platinum points—finds no ready explanation. It is possible that the metals, when melted in the wedge form, do not give way at their melting points as determined from small samples of wires. The tests

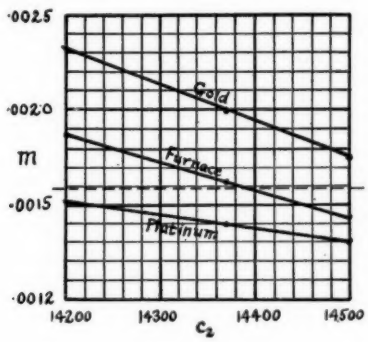


Fig. 6.

Mechanical equivalent values obtained from furnace, gold and platinum, as calculated from different values of c_2.

made at the Bureau of Standards however indicated that the melting points were not altered by the amount of metal used. Part of the discrepancy may be due to the low precision of the gold point photometric observations. The platinum point is entitled to very much greater weight for this reason.

A further possibility, not to be overlooked, is that the Planck equation may not accurately represent the radiation in the visible region at the

[12] "The Center of Gravity and Effective Wave-length of Transmission of Pyrometer Color Screens," P. D. Foote, Journal Washington Acad. of Scs., V., 15, 1915, p. 526.

temperatures involved. The discrepancy here found would fit in with this idea, but the data presented are quite inadequate to support any such claim.

In view of the unsatisfactory character of the experimental results which we have obtained, we wish to place the chief emphasis of this paper on the critical discussion of the method and on the photometric procedure which we have described and used. It is our belief that a more careful and elaborate repetition of the work than we have the facilities or the opportunity to carry out, following the lines here laid down, should result in consistent values for the mechanical equivalent of light, of an accuracy only limited by the certainty with which the laws and physical constants of the black body are known.

SUMMARY.

1. The method of obtaining the mechanical equivalent of light from the brightness of the black body has been critically discussed. It is shown that an exact value cannot be expected by this method, until the black body constants are better established than at present.

2. An experimental procedure has been outlined insuring exact correspondence between the photometric observations and the spectral luminosity curve used for calculation.

3. Using probable values for the black body constants, the mechanical equivalent of light is found, from new experiments, to lie between .00139 and .00195 watt per lumen *where "light" is defined by the spectral luminosity curve determined by the writers.*[13]

PHYSICAL LABORATORY,
THE UNITED GAS IMPROVEMENT COMPANY,
March 18, 1916.

[13] The phrase in italics is important. Of the two parts of the mechanical equivalent of light, the *lumen* is fixed by the dimensions of the present standards of luminous intensity; the *light watt* is fixed by the luminosity curve assumed. At the carbon lamp color, which is the only point which is now fixed irrespective of methods of colored photometry, the area of the light watts curve, as calculated for instance from Nutting's (experimental) luminosity curve, (which however we have not found to agree with our photometric scale), is 8 per cent. less than from our curve. Our platinum point, used with his luminosity curve, with the black body constants above chosen, gives m as .00129.

THE EFFECT OF TEMPERATURE ON THE LIGHT-SENSIBILITY CURVES OF DIFFERENT TYPES OF SELENIUM CELLS.

BY E. O. DIETERICH.

THIS paper summarizes a study of the wave-length-sensibility curves of three types of selenium cells at temperatures higher than room temperature. The investigation was begun in the early fall of 1914 and some of the results reported at the November meeting of the American Physical Society that year. The experiments, however, were interrupted and it has not been possible to complete the work as originally planned. In the meantime an article describing the effect of low temperatures on the light-sensibility curves of selenium and stibnite cells has been published by D. S. Elliott[1] who finds a behavior similar to that described below. It was thought worth while, however, to call attention to these results inasmuch as they were obtained at high temperatures and on cells of entirely different nature than those used by Elliott.

The cells used were some prepared by the writer and previously described.[2] Three types were studied: Type A, which shows no maximum in the red whatever; type C, in which the maximum in the red is lower than that in the blue; type D, in which the maximum in the red is higher than that in the blue. The permanence of the light-sensibility curves of the different types was demonstrated here; those obtained at this time were essentially the same, for the same conditions of temperature, as those obtained when the cell was first completed. Fig. 1 shows these curves for a cell of type A.

To determine the light-sensibility curves, the method outlined by Brown and Sieg[3] and previously used was followed. For obtaining the curves at temperatures higher than room temperature the cell was placed in a small oven which was about one inch square and three inches deep. This oven was constructed of plaster of Paris, wound with Nichrome wire and insulated by means of asbestos packing. It was provided with a small mica window to admit the light. By connecting it to a battery of storage

[1] PHYS. REV., Series II., Vol. V., p. 53, 1915.
[2] PHYS. REV., Series II., Vol. IV., p. 467, 1914.
[3] PHYS. REV., Series II., Vol. II., p. 487, 1913.

cells a very constant temperature could be maintained. Temperatures were measured by means of a thermometer placed directly behind the cell. At the higher temperatures the cell served as a very sensitive means of indicating variations too small to be detected on the thermometer; the resistance changing to such an extent that the galvanometer deflec-

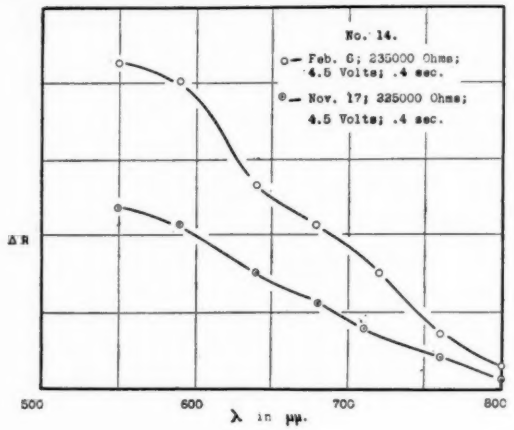


Fig. 1.

tion amounted to several hundred centimeters. Whenever possible, exposures of 0.5 sec. were taken, for with short exposures the fatigue of the cell is much less than with long exposures. However, at the higher temperatures the sensitiveness of the cells became so low that the short exposures gave galvanometer deflections too small to be read with very

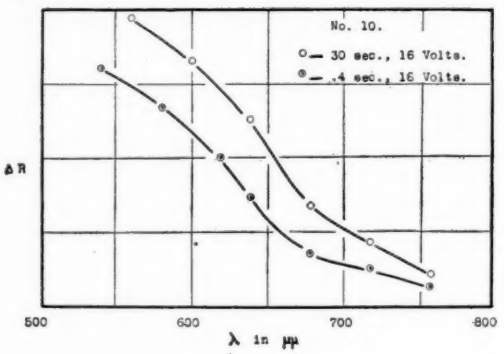


Fig. 2.

great accuracy, so here the exposures were increased in length. For certain types of cells, namely, type A, this change of period of illumination has no effect on the shape of the light-sensibility curve, as is shown in Fig. 2, where the time of illumination varies by a factor of 75. For those

cells whose light-sensibility curve depends upon the period of illumination a constant period of exposure, 10 sec., was used at all temperatures. At the higher temperatures, to increase the sensibility, higher voltages were also found necessary. It has been shown repeatedly, however, that a change of voltage does not alter the light-sensibility curves of selenium.[1]

The behavior of the various types of cells with increasing temperature is shown in Figs. 3, 4 and 5. Fig. 3 represents the curves obtained with

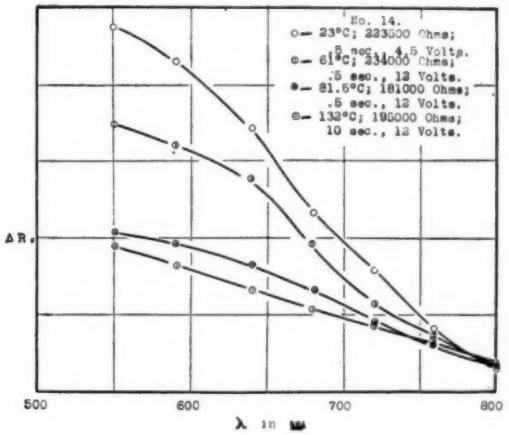


Fig. 3.

a cell of type A. The sensibility in the blue end of the spectrum decreases markedly while in the red it is hardly affected. At the highest temperature reached, however, there is no indication of an appearance of a maximum in the red, as might be expected, perhaps, as a result of the depression in the blue. Unfortunately, while trying to raise the tempera-

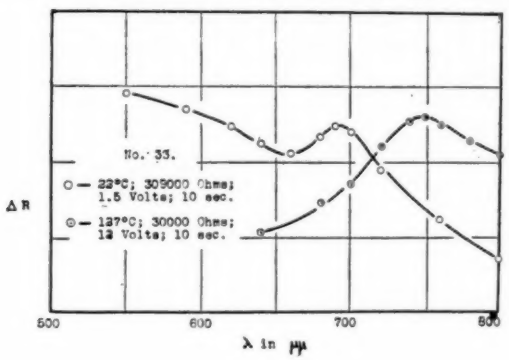


Fig. 4.

ture of this cell to somewhere near the melting point of selenium, the selenium melted and the identity of the cell was thereby destroyed.

[1] PHYS. REV., Series II., Vol. IV., p. 48, 1914.

From the behavior of cells of type A, one would be led to expect that in the case of cells with a maximum in the red, this maximum should be displaced towards the longer wave lengths. This was actually found to be the case. Figs. 4 and 5 show the progressive change of the position

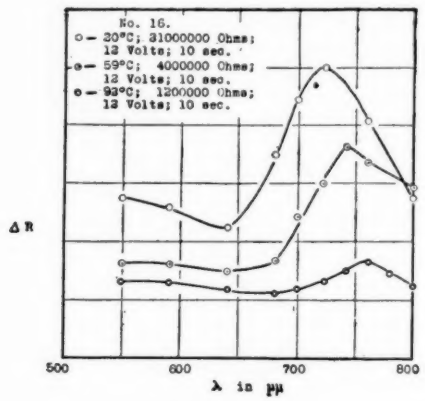


Fig. 5.

of maximum sensibility with increasing temperature. These results are in perfect agreement with those of Elliott[1] who finds the maximum shifted towards the shorter wave lengths at the temperature of liquid air.

Fig. 6 shows that the characteristic wave-length-sensibility curve at

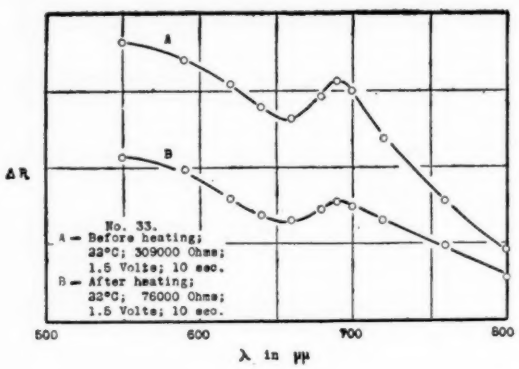


Fig. 6.

room temperature is not changed by the heat treatment; the maximum returns to the original place. The difference in resistance and sensitiveness before and after heating may probably be due to slow changes taking place in the selenium similar to those exhibited by the freshly manufactured cells.

PHYSICAL LABORATORY,
THE STATE UNIVERSITY OF IOWA.

[1] PHYS. REV., Series II., Vol. V., p. 53, 1915.

THE MEASUREMENT OF TIME WITH A MOVING COIL GALVANOMETER.

BY PAUL E. KLOPSTEG.

I. INTRODUCTION.

THE well-known method of measuring the time occupied by events of very short duration by means of the ballistic galvanometer[1] depends upon the relation between electrical quantity and current, and upon the fact that for sudden discharges the throws of the galvanometer coil are proportional to the quantities which have passed. Essentially this is the method described by Brown,[2] who used an unbalanced Wheatstone net[3] for applying the potential differences to the galvanometer terminals. The observed proportionality between throws and time intervals up to three seconds was obviously due to the fact that his galvanometer had a period of 91 seconds. The reliability of his absolute measurements was about 2.5 per cent., the amount of the discrepancy between the two values of the ballistic constant as determined by two different methods.

When an event lasting but six or seven seconds or less is to be measured with a fair degree of accuracy, a stop watch, because of its mechanical limitations and the large probable error in starting and stopping, is out of the question. It is not to be gainsaid that a method, employing simple apparatus, with which such intervals might be measured with an error not exceeding several thousandths of a second, would prove valuable; in many experiments it could be used in place of a chronoscope or high speed chronograph with standard clock. The chief objection to using a long period galvanometer for this purpose, in which the discharge has stopped before the coil has moved appreciably,[4] is the tax on the experimenter's patience in having to wait until the instrument is ready for the next deflection. To employ a short period galvanometer for a time measurement requires that the current, impressed during the interval to be timed, shall flow while the coil is moving, and that the interval be

[1] Kohlrausch, Lehrb. d. prakt. Phys., 12th ed., p. 527.

[2] Brown, F. C., PHYS. REV., O.S., 34, 452, 1912.

[3] The Wheatstone net is not essential to the method. A simpler means of applying the potential difference to the galvanometer would simplify his equations (5) and (6), p. 453.

[4] This is the assumption upon which the ordinary ballistic measurement, in which throws and quantities are taken proportional, is based.

deducible from the observed elongation. It is the purpose of this paper to derive the relationship involved. Dorn,[1] Diesselhorst,[2] Peirce[3] and Worthing[4] have treated the inverse of this problem for quantities obeying various laws of discharge, the two last named for the moving coil type of instrument.

II. THEORETICAL.

A. *General Outline of Method of Derivation.—Notations.*

In the development of the theory underlying the method, the well-known type of instrument with an open rectangular coil having no auxiliary damping devices, and moving coaxially about an iron core between two magnetic poles, will be considered. Briefly, the method of deduction for any condition of damping, may be outlined as follows:

1. From the equation of its motion, the position and angular velocity of the coil, initially at rest, are determined for a particular instant τ seconds after a steady current has begun flowing through the instrument.

2. These respective values of position and angular velocity are introduced as initial conditions into the equation of motion of the coil, swinging without resultant torque, corresponding to the condition that at the instant τ the current was cut off.

3. From the resulting equation is found, in the usual manner, the maximum angle of displacement; the expression for this angle is to be solved for τ.

On account of their presumable applicability the two cases of slightly damped and of critically damped motions, respectively, will be treated, with the aid of the following notations:

τ = time interval to be measured;
θ = angular displacement of coil at time t;
I_0 = moment of inertia of coil;
$2f$ = proportionality constant between damping moment and angular velocity of coil;
$M = nAH$, where n is the number of turns and A the mean area of the coil, and H = average field intensity;
q^2 = elastic torque constant of suspensions;
i = steady current impressed upon circuit;
T_0 = period[5] of undamped coil;
T = period of damped coil;

[1] Dorn, E., Wied. Ann., 17, 654, 1882.

[2] Diesselhorst, H., Ann. d. Phys., 9, 712, 1902.

[3] Peirce, Am. Acad. Proc., 44, 283, 1909.

[4] Worthing, A. G., PHYS. REV., N. S., 6, 165, 1915.

[5] In this paper the term "period" refers to the time of a complete or double vibration of the coil.

ρ = ratio between successive elongations;
Λ = logarithmic decrement;
k = current constant of coil;
α, β, γ = respective throws in undamped, damped periodic, and critically damped motions of the coil; with subscript τ the throws represented are due to current i for time τ; with subscript i, the throws are due to the same quantity, $i\tau$, instantaneously discharged.

$$\Lambda' = \frac{\Lambda}{\sqrt{1 + \frac{\Lambda^2}{\pi^2}}}.$$

Other symbols to be used are better explained at the points where they are to be introduced.

B. *Damped Periodic Motion.*

(*a*) *Derivation.*—Following the plan of procedure as outlined, we have

$$\theta_\tau = \frac{Mi}{q^2}\left[1 - \epsilon^{-a\tau}\left(\cos b\tau + \frac{a}{b}\sin b\tau\right)\right], \tag{1}$$

and

$$\omega_\tau = \frac{Mi}{q^2}\epsilon^{-a\tau}\left[\left(b - \frac{a^2}{b}\right)\sin bt - 2a\cos b\tau\right]. \tag{2}$$

Equations (1) and (2) give, respectively, the angular position and velocity of the coil at the instant the current is cut off. In these equations

$$a = f/I_0$$

and

$$b = \sqrt{\frac{q^2}{I_0} - \frac{f^2}{I_0^2}}.$$

The next step is to find the elongation which the coil will attain by virtue of its angular momentum at this instant.

The general equation for the motion of the coil when there is no torque tending to displace it permanently from its position of the rest is

$$\theta = \epsilon^{-at}(A\cos bt + B\sin bt), \tag{3}$$

where a and b have the same values as before, because experimentally it is possible so to arrange the circuits[1] that exactly the same conditions of damping obtain when the electromotive force is applied as when it is cut off. A and B are the constants of integration, which are to be evaluated by introducing the conditions that at $t = 0$, $\theta = \theta_\tau$ and $d\theta/dt = \omega_\tau$. The equation then becomes

[1] For example, as shown in Fig. 2 of this paper.

$$\theta = \epsilon^{-at}\left(\theta_\tau \cos bt + \frac{\omega_\tau + a\theta_\tau}{b} \sin bt\right). \tag{4}$$

By the usual method it is found that the direction of motion of the coil reverses for the first time at the instant

$$t_1 = \frac{1}{b}\tan^{-1}\left[\frac{\omega_\tau b}{a\omega_\tau + (b^2 + a)\theta_\tau}\right], \tag{5}$$

and that the corresponding elongation (designating the expression in brackets by ψ) is

$$\beta_\tau = \epsilon^{-\frac{a}{b}\tan^{-1}\psi}\left(\theta_\tau \cos \tan^{-1}\psi + \frac{\omega_\tau + a\theta_\tau}{b} \sin \tan^{-1}\psi\right). \tag{6}$$

Obviously, we might now proceed to substitute, first for ψ, and then for θ_τ and ω_τ, the values given, respectively, by equations (5), (1) and (2); the resulting equation would involve τ, the quantity sought, β_τ, the quantity observed, and others, all of which, with the exception of τ, are directly determinable. The equation would not, however, be an explicit solution for τ, which would necessitate a graphical method or development in a series with resulting approximations, in order to find the interval. Hence, to obtain a practicable formula explicitly solved for τ, we may proceed as is done in the derivation of the formula for the ballistic constant when damping is small: disregard damping in the derivation and introduce the damping correction after the formula for undamped motion has been obtained. Thus, setting $f = 0$ in the preceding equations, (6) reduces to

$$\alpha_\tau = \frac{Mi}{q^2} \cdot 2 \sin \frac{\pi\tau}{T_0}, \tag{7}$$

from which

$$\tau = \frac{T_0}{\pi}\sin^{-1}\frac{k}{2i}\alpha_\tau. \tag{8}$$

Introducing the damping correction, damping being assumed small,[1]

$$\tau = \frac{T}{\pi}\sin^{-1}\frac{k}{2i}\beta_\tau \sqrt{\rho}. \tag{9}$$

(*b*) *Discussion. Sources of Error and Precautions.*—Formula (9) may be used as it stands for measurement of time intervals less than the half period of the coil. The factor which gives rise to the greatest uncertainty in the results is the current constant,[2] which is not the same at all deflections, principally on account of non-homogeneity in the magnetic field of the instrument and probable imperfect leveling. However, the

[1] Klopsteg, PHYS. REV., N. S., 7, 543, 1916.

[2] Kloptseg, Phys. Rev., N. S., 7, 633, 1916.

field about the coil in its usual equilibrium position is fairly uniform within a region corresponding to a deflection of about 6 cm. on each side of the null position, on a scale at 50 cm. from the mirror. The error in the constant may therefore be minimized by shifting the coil, by means of the upper torsion head, to a position about 6 cm. to one side of the usual null point, using this as a new zero setting, the deflections from which are kept within 12 cm., i. e., within 6 cm. beyond the former zero of the scale. This manipulation also largely eliminates the zero shift due to magnetic impurities.[1] It has been shown that a small twist in the suspensions produces no change in the current constant, provided the field be uniform.[2]

(*c*) *Modified Form of Equation* (*10*).—To obviate much of the labor of computation involved when equation (9) is used for the determination of a number of intervals of different durations, we may make this equation the basis of a graphical method. By equation (7) it is seen that, for zero damping,

$$\frac{\alpha_\tau}{\phi} = 2 \sin x, \tag{10}$$

where ϕ is the steady deflection produced by the same current which is used in obtaining the throw,[3] and x is written in place of $\pi\tau/T_0$. Making use of the formula for the ballistic constant $K = T_0 k/2\pi$, equation (7) may be written

$$\alpha_i = \alpha_\tau \frac{x}{\sin x}, \tag{11}$$

which remains true when α is replaced by β. Thus, if we plot $2 \sin x$ as abscissas and $x/\sin x$ as ordinates we obtain a correction curve which enables us, from a given throw in terms of the angle of steady deflection with the same current, to obtain the correction factor by which this throw must be multiplied in order to give the throw which would have been produced by the same quantity, instantaneously discharged. Inasmuch as the damping factor has not been introduced into the curve, the latter is applicable to any instrument whatseover, after the observed throws have been reduced to the equivalent undamped throws. When the equivalent "instantaneous throw" has been obtained, the damping factor may be applied, and τ found by the simple relation

[1] Zeleny, A., PHYS. REV., O. S., 32, 297, 1911.

[2] Loc. cit.

[3] When short intervals are measured it may not be feasible to produce this steady deflection directly on account of the large current which must be used to obtain a throw of sufficient magnitude. In this case ϕ is calculated from the current constant obtained with a small current.

$$\tau = \frac{T}{2\pi}\frac{\beta_i}{\phi}\sqrt{\rho}, \tag{12}$$

which may also be written

$$\tau = \frac{K}{i}\beta_i. \tag{13}$$

The form (13) eliminates the necessity of making a direct time determination.

(*d*) *Effect of Prolonged Steady Discharge upon Throw.*—Equation (11) enables us to determine the error made in assuming a quantity of electricity, flowing uniformly, to have passed through the coil in a negligibly short interval, the discharge having actually been prolonged through an interval τ. The correction factor,[1] as has been seen, is $x/\sin x$, which is independent of the damping factor over a wide range of conditions. It does not, however, apply with exactness to critically damped motion, as will be shown later. Equation (11) shows that the error committed in any measurement is theoretically less than 0.2 per cent. if the interval measured is less than about $T/30$. Applying this to a galvanometer of 91 seconds' period, like the one used by Brown, the discharge may be allowed to pass a trifle over 3 seconds without introducing appreciable error into the measurement. The results cited by Brown are in conformity with this conclusion.

C. *Critically Damped Motion.*

(*a*) *Derivation.*—The same procedure will be followed as in the case of periodic motion, except that no assumptions as to damping need be made. The final formula is theoretically accurate.

Corresponding to equation (1), we have

$$\theta_\tau = \frac{Mi}{q^2}[1 - \epsilon^{-a\tau}(1 + a\tau)]; \tag{14}$$

and to equation (2),

$$\omega_\tau = \frac{Mi}{q^2}a^2\,\tau\epsilon^{-a\tau}. \tag{15}$$

When the resultant displacing torque is zero, the equation of motion is

$$\theta = \epsilon^{-at}(A + Bt), \tag{16}$$

and, imposing the same initial conditions as upon equation (3),

[1] The expression given by Diesselhorst (*l. c.*) for a prolonged steady current, reduced to the notation of this paper, is $\alpha_\tau = \alpha_i(1 - (x^2/6))$. The corresponding form of eq. (11) is $\alpha_\tau = \alpha_i(\sin x)/x$; expanding $\sin x/x$, we obtain $1 - (x^2/3!) + (x^4/4!) \cdots$, which shows Diesselhorst's correction to be identical with the first two terms of the series found. This is sufficiently accurate for the shorter intervals.

$$\theta = \epsilon^{-at}[\theta_\tau + (\omega_\tau + a\theta_\tau)t]. \tag{17}$$

The maximum of this function occurs at the instant

$$t_c = \frac{1}{a\left(1 + a\frac{\theta_\tau}{\omega_\tau}\right)}, \tag{18}$$

and its value is, corresponding to equation (6),

$$\gamma_\tau = \epsilon^{-\frac{1}{1+a\frac{\theta_\tau}{\omega_\tau}}}\left(\theta_\tau + \frac{\omega_\tau}{a}\right). \tag{19}$$

Inserting the values of θ_τ and ω_τ, and expressing the results in terms of the ratio of the observed throw to the steady deflection with the same current,

$$\frac{\gamma_\tau}{\phi} = \frac{\epsilon^{2x} - 1}{\epsilon^{2x\left(\frac{\epsilon^{2x}}{\epsilon^{2x}-1}\right)}}, \tag{20}$$

where x has the same significance as before.
For critical damping we have[1]

$$\frac{\gamma_i}{\phi} = \frac{2x}{\epsilon}. \tag{21}$$

Let the factor by which the observed throw must be multiplied in order to reduce it to the equivalent throw resulting from an instantaneous discharge with the same quantity be represented by δ; then

$$\delta = \frac{2x}{\epsilon} \cdot \frac{\epsilon^{2x\left(\frac{\epsilon^{2x}}{\epsilon^{2x}-1}\right)}}{\epsilon^{2x} - 1}. \tag{22}$$

From (20) and (22) are obtainable corresponding values of γ_τ/ϕ and δ, for various assigned values of $2x$. The curve of Fig. 1 is plotted with

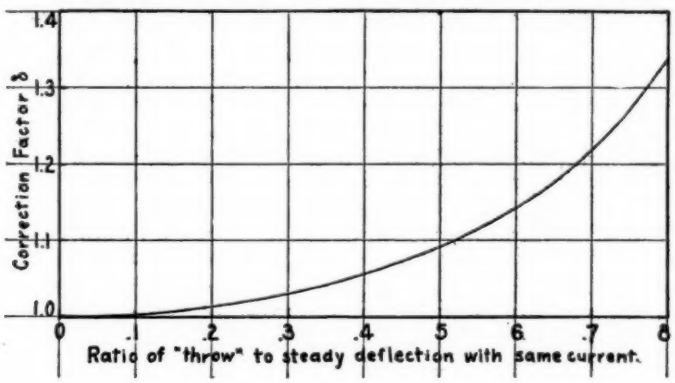


Fig. 1.

[1] The value of a in this case is $1/t_1$, where t_1 is the duration of the throw produced by an instantaneous discharge. Its value in terms of the undamped period is $T_0/2\pi$.

γ_τ/ϕ as abscissas and δ as ordinates, and Table I. gives the values from which this correction curve may accurately be plotted. This method of treatment is, in this case, unavoidable, because of the implicit appearance of τ in equation (20).

TABLE I.

$2x$	γ_τ/ϕ	δ	$2x$	γ_τ/ϕ	δ
0.00	0.0000	1.0000	1.60	0.5325	1.1055
0.05	0.0184	1.0002	1.65	0.5458	1.1121
0.10	0.0368	1.0004	1.70	0.5590	1.1189
0.15	0.0551	1.0010	1.75	0.5718	1.1259
0.20	0.0734	1.0017	1.80	0.5845	1.1330
0.25	0.0917	1.0026	1.85	0.5968	1.1404
0.30	0.1099	1.0038	1.90	0.6089	1.1479
0.35	0.1281	1.0051	1.95	0.6207	1.1557
0.40	0.1462	1.0067	2.00	0.6323	1.1636
0.45	0.1642	1.0084	2.05	0.6436	1.1717
0.50	0.1820	1.0104	2.10	0.6547	1.1801
0.55	0.1998	1.0126	2.15	0.6654	1.1887
0.60	0.2175	1.0149	2.20	0.6760	1.1973
0.65	0.2350	1.0175	2.25	0.6863	1.2061
0.70	0.2524	1.0204	2.30	0.6963	1.2152
0.75	0.2696	1.0234	2.35	0.7060	1.2244
0.80	0.2867	1.0266	2.40	0.7156	1.2338
0.85	0.3036	1.0300	2.45	0.7249	1.2434
0.90	0.3203	1.0336	2.50	0.7339	1.2532
0.95	0.3369	1.0375	2.55	0.7428	1.2630
1.00	0.3532	1.0415	2.60	0.7516	1.2729
1.05	0.3694	1.0457	2.65	0.7598	1.2831
1.10	0.3854	1.0501	2.70	0.7680	1.2934
1.15	0.4011	1.0548	2.75	0.7759	1.3039
1.20	0.4166	1.0596	2.80	0.7836	1.3146
1.25	0.4319	1.0647	2.85	0.7910	1.3254
1.30	0.4470	1.0699	2.90	0.7982	1.3365
1.35	0.4618	1.0754	2.95	0.8052	1.3478
1.40	0.4765	1.0810	3.00	0.8122	1.3592
1.45	0.4908	1.0868	3.05	0.8186	1.3707
1.50	0.5050	1.0928	3.10	0.8251	1.3824
1.55	0.5188	1.0990	3.15	0.8312	1.3942

(*b*) *Application of Method and Precautions.*—The procedure in making a determination of an interval by this method is exactly like that outlined in Part B, Sec. *c* above, except that the damping factor is now included. Having determined γ_τ/ϕ, δ is found from the table or curve; the product of these two quantities is γ_i/ϕ, which is substituted in

$$\tau = \frac{\epsilon}{2\pi} T_0 \frac{\gamma_i}{\phi}. \qquad (23)$$

Equation (23) may also be written in a form analogous to (13):

$$\tau = \frac{K}{i}\gamma_i. \tag{24}$$

Here, as before, K is the ballistic constant of the instrument;[1] and this form of the equation does away with the necessity of making a direct determination of time. The precautions mentioned, in connection with the other method, for minimizing error due to non-uniformity of the magnetic field, should be observed.

(*c*) *Production of Damping Exactly Critical.*—Because damping is so significant at the boundary condition between periodic and aperiodic motion in determining the magnitude of the throw, it is important that the resistance in shunt with the galvanometer be so adjusted as to render damping exactly critical. Wenner[2] has given an empirical method which is useful when exactness of conditions is not important; by its means the critical damping resistance may be determined with an accuracy of perhaps 5 per cent., which is sufficiently close for many purposes. It might appear that the simplest way would be to observe the motion of the coil directly and adjust the resistance until the desired condition is reached. The writer's experience is, however, that damping is invariably overestimated; one cannot distinguish in the ordinary galvanometer between a logarithmic decrement of, say 7, and an infinite logarithmic decrement.

A method of adjusting the resistance of the shunt to an accuracy of a small fraction of a per cent. is developed elsewhere.[3] It is given by the formula

$$r_c = r_1 \frac{\Lambda_1' - \lambda}{\pi - \lambda}, \tag{25}$$

where r_c is the total resistance in the galvanometer circuit at which damping is critical; r_1 is the total resistance in the circuit to which corresponds the logarithmic decrement Λ_1; and λ is the logarithmic decrement on open circuit. If the latter is great, λ' should be used.[4]

D. *Measurable Intervals.*

A consideration of the formulas shows that the method which makes use of the slightly damped galvanometer should prove useful for timing any event the duration of which is less than the half period of the coil. In the method of critically damped motion, there is, according to the formula, no upper limit; but when the "throw" approaches the

[1] The ballistic constant in critical damping is equal to $\epsilon T_0 k/2\pi$.

[2] Wenner, F., PHYS. REV., O.S., 22, 192, 1906.

[3] Klopsteg, Dissertation, Minn., 1916. See also Jaeger, Z.S. f. Instrk., 23, 266, 1903.

[4] For significance of primed logarithmic decrements, see table of notations.

steady deflection in magnitude, the increase of deflection per second is small. Greater intervals than the half period of the undamped coil should, however, be accurately measurable, since when $\tau = T_0/2$, the angle of deflection is only 83 per cent. of the final steady deflection, as Table I. shows. In both cases the upper limit may obviously be extended by increasing the moment of inertia of the coil;[1] this is preferable to diminishing the torsional control, since weak control means large possible variation in damping factor and unsteady zero. When the method of critical damping is used, the relation between moment of inertia and controlling torque should be such that some external resistance is required to make damping critical; this minimizes error due to fluctuations of resistance of the coil with varying temperature.

The suggestion lies near at hand to employ the equations developed for calibrating the scale of a particular instrument which, let us say, is in a fixed position and has been adjusted once for all, so as to make it direct reading for time. The author hopes to determine the practicability of this suggestion in the near future.

III. EXPERIMENTAL.

A. *Description of Apparatus.*

To verify the theory which leads to the equations for the measurement of time by this method, a Leeds and Northrup P type galvanometer having a resistance of 126.3 ohms was used. The coil was suspended by a 1.5-mil

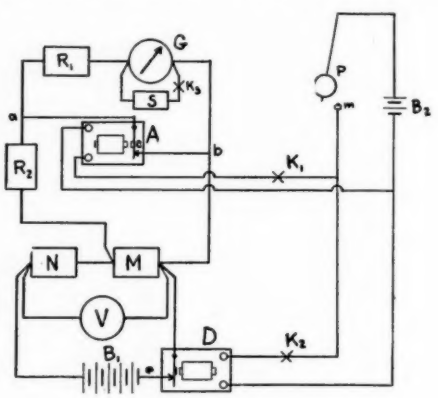


Fig. 2.

phosphor bronze strip. The connections were made as indicated in Fig. 2. G is the galvanometer and S is the shunt by means of which, upon

[1] Zeleny, A., PHYS. REV., O.S., 23, 404, 1906; Peirce, B.O., Am. Acad. Proc., 44, 287, 1909.

closing the switch K_3 the instrument can be damped critically. The portion *acb* of the circuit serves to short-circuit the instrument; the resistance R_1 renders the resistance of *acb* vanishingly small compared with that of the upper branch. R_2 is a resistance of such large value that the logarithmic decrement remains small. M and N, with the voltmeter V and the battery B_1 constitute a potentiometer arrangement permitting a current of any desired strength to be sent through the galvanometer. A and D are relays, which may, at will, be connected through the switches K_1 and K_2, respectively, to the clock circuit containing the seconds pendulum P and the battery B_2. The relays are so adjusted as to stick after a momentary current has passed through them, thus breaking the circuit and keeping it open until set by hand for the next determination. It is noticed that the beginning and end of the interval are each marked by the breaking of a circuit, this being more reliable than first to "make" the circuit through the galvanometer and then to break it. The arrangement in the figure, furthermore, keeps the logarithmic decrement of the coil constant whether or not a current is flowing.

With these connections it is possible to keep the current flowing through the galvanometer during any desired whole number of seconds, simply by proper timing of the instants of closing the switches K_1 and K_2.

B. *Results from Method of Periodic Motion.*

Two representative sets of determinations to verify equation (10) are given in Table II., Columns II. and III. There is an indication of falling off of accuracy in the sixth second, which is to be expected, inasmuch as the half period of the coil is 6.5 seconds. The manipulation is somewhat more difficult than that of using the galvanometer for the measurement of instantaneous discharges, since, for the longer intervals, throws may not be taken without bringing the coil quite to rest.[1]

C. *Results from Method of Critically Damped Motion.*

Table II., Column IV., shows results obtained by means of equation (23) in connection with Table I. It is the writer's experience in repeated tests of both methods that this is the more satisfactory to work with, both as regards ease of manipulation and simplicity of making the computation when the table of values for δ is available. In fact, one may feel confident of being able to obtain a certain set of observations by this method in half the time required by the other, and that with greater accuracy, as a comparison of columns II. and III. with column IV. indicates.

[1] Zeleny, A., PHYS. REV., O.S., 23, 405, 1906.

TABLE II.

I.	II.	III.	IV.
1.000	1.002	1.000	1.001
2.000	2.004	2.004	2.000
3.000	3.009	3.000	3.001
4.000	3.998	4.008	3.994
5.000	4.996	5.008	5.000
6.000	5.968	6.038	6.006

I.: Actual seconds by standard clock. II. and III.: Time determined by means of equation (10). IV.: Time determined by means of equation (23) and Table I. Period of coil: 13.02 sec.; critical damping resistance, 255.4 ohms.

As has been pointed out earlier, the critical damping resistance should be accurately adjusted. The following determinations made in connection with the results of Table II. will indicate the reliability of the method of equation (25) for finding that resistance.

$G = 126.3\Omega \qquad \lambda = 0.0411 \qquad \pi - \lambda = 3.100$

r_1	Δ_1'	$\Delta_1' - \lambda$	r_c	
10,000	0.1590	0.1179	380.5	Average $r_c = 381.7\Omega$
9,000	0.1726	0.1315	381.8	$S = 381.7 - 126.3 = 255.4\Omega$
7,000	0.2107	0.1696	382.8	

IV. SUMMARY.

1. A method is developed for the measurement of time intervals by means of a short period galvanometer under two conditions of damping, viz.: slight damping and critical damping. It depends upon the elongation resulting from a steady current sent through the instrument during the interval to be measured.

2. The first method may be used for intervals approaching the half period of the coil, with an accuracy of about 0.3 per cent.

3. The method which makes use of the critically damped condition is useful for intervals of at least the same length, with an accuracy which is dependable to almost 0.1 per cent., provided a shunt of proper resistance is used to make damping exactly critical. A table is given which simplifies the calculations of this method.

4. An equation is given by means of which the critical damping resistance may accurately be determined.

It is a pleasure to acknowledge suggestions received from various members of the staff of this laboratory, which have materially aided in facilitating the progress of this work.

PHYSICAL LABORATORY,
UNIVERSITY OF MINNESOTA,
March 24, 1916.

PHENOMENA ATTENDING THE PASSAGE OF X-RAYS THROUGH NARROW APERTURES.

BY E. G. TAYLOR.

IN the Phys. Zeit. of 1914 there appeared an account of a series of experiments made by J. Laub dealing with the phenomena attending the passage of X-rays through narrow apertures. Later in the Ver. Hand. Deut. Phys. Ges., p. 354, 1915, he reviewed the work done and there advanced a hypothesis for the explanation of the phenomena observed.

In these experiments X-rays were allowed to pass the boundaries of various opaque substances and fall upon a photographic plate a few centimeters distant. As a result of this, there appeared upon the photographic plate a perfectly definite set of parallel lines separated by areas of minimum intensity in the region shielded from the direct action of the rays.

In one experiment the X-rays were passed obliquely through a circular aperture in a lead screen and produced a series of bands concentric with the aperture. In a similar experiment X-rays were passed through a narrow rectangular aperture 0.3 mm. wide in a thick lead screen. The photographic plate in this case showed a central image of the aperture with a symmetrical set of bands on each side. The general appearance was the same as when ordinary light passes an aperture and produces diffraction bands.

The hypothesis advanced by Laub assumed that in the mechanical production of the apertures micro-crystalline structures were formed on the aperture surface and the X-rays were diffracted by these crystals.

A much simpler alternative hypothesis occurred to us as doubtless to many others and it seemed worth while to decide between the two. Some of Laub's experiments were accordingly repeated in this laboratory. A rectangular aperture 0.3 mm. wide in a lead sheet 1 cm. thick was placed 28 cm. from the anticathode of a Cooledge Tube. The photographic plate was placed 35 centimeters distant from the aperture and a series of linear bands were produced which closely resembled those of Laub. It was then found that if a lead screen with a slit 0.6 mm. wide was placed between the aperture and the tube 8 cm. from the focal region, thereby reducing the focal area used, the bands were entirely

eliminated. This was entirely consistent with our hypothesis that Laub's bands were astigmatic "pinhole" or "*slithole*" images of the bright regions of the focal area on the anticathode.

By taking pinhole images of the focal region it was found that this region showed a series of radiating areas elliptical in contour with very intense sources at the foci. There was an exact geometrical correspondence between these intense foci and the strongest linear bands previously obtained. To make the evidence more complete we then substituted a 0.3 mm. slit with iron faces for the lead slit previously used, removing the lead diaphragm nearest the tube. The other conditions were as before: potential 55,000 volts, current 2.5 milliamperes and time of exposure 5 hours. The result of this experiment was a set of bands identical with those obtained by using the single rectangular lead aperture.

These data satisfactorily show that the bands are the astigmatic slit-hole images of radiating areas of unequal intensity in the focal region, and are not due to diffraction from a micro-crystalline structure as suggested by Laub, since it is highly improbable that such elements as iron and lead should possess the same micro-crystalline structure. The same hypothesis also serves to explain the origin of the concentric bands observed by using a circular aperture.

We have also repeated one other experiment of Laub's which involved the passage of X-rays through a rather large aperture in a lead screen, Phys. Zeit., 1914, p. 730. While our photographs do not show the fine lines which appear in Laub's drawing, they do show some of the same characteristics, such as a doubling of the edges, and certain apparent minima. The pecularities of our photographs are all explicable upon the projection hypothesis already outlined, and it seems highly probable in the light of what we have already shown that if we knew the distribution of X-ray sources in Laub's tube, the corresponding features of his photograph could be similarly accounted for. Without having been able to repeat all of Laub's observations, we feel that that we have sufficient data to warrant the conclusion that his results were not due to micro-crystalline structures, but were relatively simple consequences of the geometrical relation of aperture, plate and X-ray sources in his tube.

DEPARTMENT OF PHYSICS,
UNIVERSITY OF WISCONSIN,
May 5, 1916.